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PLANT OPERATIONS FINAL REPORT: CO_2 ACCEPTOR
PROCESS GASIFICATION PILOT PLANT

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NOTICE

PLANT OPERATIONS FINAL REPORT

CO$_2$ ACCEPTOR PROCESS
GASIFICATION
PILOT PLANT

FINAL REPORT
VOLUME 12, BOOK 2 OF 4
PERIOD: JANUARY 1972 - OCTOBER 1977

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Page

SECTION 5
PROCESS PERFORMANCE - GASIFICATION SYSTEM

LIST OF FIGURES

SECTION 5
PROCESS PERFORMANCE - GASIFICATION SYSTEM

SECTION 5
PROCESS PERFORMANCE - GASIFICATION SYSTEM

LIST OF TABLES (continued)

SECTION 5

PROCESS PERFORMANCE - GASIFICATION SYSTEM

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PROCESS PERFORMANCE - GASIFICATION SYSTEM

The results of the gasification pilot plant operation are reviewed in this section. A brief tabular history which summarizes the pilot plant objectives, major problems encountered, and the accomplishments of each run is presented for reader convenience. Because an understanding of particle and fluid dynamics is critical to the design and optimization of the CO_2 acceptor process, much effort is devoted to the analysis of solids fluidization, solids transport, and system pressure balance. Most importantly, heat and material balances for selected runs, during which steady-state pilot plant operation was achieved, are presented to aid in appraisal of the process.

The pilot plant operating program began in April, 1972, and ended with the completion of the last run on October 1, 1977. A total of 75 runs were completed in which over 6,400 hours of operating time were logged while at design process temperature and pressure. Over 6,500 tons of dry lignite and subbituminous coal were gasified. Three North Dakota lignites (Velva, Glenharold, and Husky), one Texas lignite, and three subbituminous coals (Sarpy Creek and Rosebud (Montana) and Wyodak (Wyoming)) were successfully gasified.

Twelve detailed heat and material balances were obtained which demonstrate the adaptability of the CO_2 acceptor process to a wide range of feedstocks, including lignites for which no other known process can be adapted. A discussion of the heat and material balances is given in Subsection 5.3.6.

The CO_2 acceptor process pilot plant was the first of the second generation gasification processes to undergo a comprehensive environmental characterization study. This study, as reported in Volume 11 of this report, validates all of the claimed advantages of the CO_2 acceptor process and reveals that the process can be operated in an environmentally acceptable manner with present control technology.

5.1 RUN HISTORIES

A brief summary of each of the 75 runs conducted in the pilot plant is listed in Table 5-1. A more detailed account of each run is given in the individual run reports published in Volume 8 of this report.

5.2 SOLIDS TRANSPORT

This section is concerned with providing pertinent information about the behavior of the fluidized beds maintained in regenerator and gasifier vessels of the CO_2 acceptor gasification process. The interpretation and use of differential pressure measurements for determining fluidized bed density, height, and char-acceptor interface level are discussed; as well as the measurement of the acceptor circulation rate, the transfer of solids through standlegs and lift lines, and the establishment and control of proper system pressure balance.

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next-Run
1A	4/5/72- 4/11/72	150	0	0	None	0	Achieve integrated Pilot Plant operation.	Completed system pressure test. Established dolomite inventory and calcined $MgCO_3$ portion of acceptor.	Leak in pressure probe in gasifier bed.	Inability to read dolomite level in gasifier boot.	Removed vertical pressure probe from gasifier and installed side taps in gasifier and regenerator.
1B	4/15/72- 4/25/72	190	0	0	None	0	Achieve integrated Pilot Plant operation.	Established dolomite acceptor inventory and dolomite circulation (unstable) between the regenerator and gasifier.	Pressure taps in spent dolomite transfer line continually plugged.	Relief valve on inert gas holder failed causing regenerator and gasifier beds to slump and acceptor lift line to plug.	Inert gas system repaired and tested.
2	6/3/72- 6/9/72	160	0	0	None	0	Achieve integrated Pilot Plant operation.	Established dolomite acceptor inventory and achieved 14 hours of stable dolomite circulation between vessels.	(1) Pressure taps on gasifier and regenerator continually plugged. (2) Solids accumulated at inlets to gasifier and regenerator quench towers.	Blind in vent line to flare stack was not removed after construction was completed. Gas was venting through a water drain line on the flare. Closing the valve on this line caused the gasifier pressure to increase and subsequent opening shocked the system and caused a shutdown.	(1) Revised side pressure taps to 1/2-inch pipe with rod out assemblies. (2) Reinstalled gasifier pressure probe using 1/2-inch rather than 1/4-inch tubing for sensing lines.

Table 5-1. RUN HISTORIES

2

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
3	7/10/72- 7/19/72	205	0	0	Husky Char	0	Achieve integrated Pilot Plant operation.	Established acceptor inventory, circulation and maintained plant pressure balance.	(1) Gasifier bed pressure differential distorted by leaks in impulse lines. (2) Plugs were experienced in char inlet line to the gasifier.	Acceptor lift line ruptured.	Replaced acceptor lift line as per original design. Revised start-up procedure to insure the absence of oxygen in the acceptor lift gas prior to starting circulation.
4	8/10/72- 8/20/72	180	0	0	Husky Char	0	Achieve integrated Pilot Plant operation.	Established gasifier char bed and initiated fuel char combustion in the regenerator.	(1) Inability to transfer dolomite from gasifier boot to regenerator or dolomite dump hopper, F-213. (2) Experienced difficulties transferring dolomite from gasifier to engager pot. (3) Difficulty in maintaining seal on char lift line.	(1) Solids plug in gasifier (2) Acceptor lift line plugged. (3) Char lift line plugged with dolomite and char.	After the third shutdown, it was observed that gas was bypassing the gasifier bed through cracks in the boot refractory. All refractory in the gasifier boot and transition section was replaced.
5	10/9/72- 11/1/72	380	0	0	Husky Char	0	Achieve integrated Pilot Plant operation.	Attained 1750°F calcining temperature.	Numerous upsets in quench systems.	Regenerator refractory failure. Increasing frequency of upsets in quench systems.	Replaced refractory in regenerator.

Table 5-1. RUN HISTORIES (continued)

3

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
6	12/5/72-1/28/73	0	0	0	0	0	Perform special fluidized bed tests in the gasifier and in a glass fluid bed model.	Tests provided information which allowed relating the differential pressure measurements across fluidized beds to the actual fluid bed behavior. Interface stability and acceptor showering were also studied.	Line between Gasifier and spent acceptor dump hopper plugged several times. Sulfur corrosion of the gasifier recycle gas heaters continued to be a problem.	Scheduled.	Revised startup and operating procedures based on data obtained from fluidization tests.
7	2/12/73-3/11/73	380	7	0	Husky Char	0	Achieve integrated Pilot Plant operation.	Used natural gas for the first time as an auxiliary fuel, achieved complete calcination of the regenerator acceptor inventory.	Line plugs, loss of interface in gasifier. Temperature and pressure probe in regenerator broke.	Agglomeration of solids in gasifier.	Installed ring type distributor in transition of gasifier. Revised operating procedure to include addition of air to gasifier side.
8	3/28/73-4/10/73	240	10	0	Husky Char	0	Achieve integrated Pilot Plant operation.	The run demonstrated that the gasifier char bed could be partially gasified and the char bed density reduced by injecting an air steam mixture through the raw side flow gas distributor.	Hot spots on solids transfer lines caused by broken end plates. Agglomeration of acceptor in regenerator. Plugging at inlet to regenerator quench tower. Heater tubes deteriorating from sulfur corrosion.	Tube ruptured in regenerator air heater.	Repaired heater tubes. Installed ring type gas distributor in regenerator.

4

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
9	4/14/73-4/19/73	40	13	0	Husky Char	0	Achieve integrated Pilot Plant operation.	Greatly improved regenerator fuel char transfer reliability by redesigning the fuel char flow control system.	Hot spots of side flow line to gasifier high pressure drop across gasifier recycle gas heater. Agglomeration of acceptor in regenerator.	Plug in acceptor lift line.	Revised operating procedure to include use of hot potassium carbonate system to remove carbon dioxide from regenerator recycle gas.
10A	5/18/73-5/23/73	112	3	2	Husky Char	1,000	Achieve integrated Pilot Plant operation.	Achieved fully integrated plant operation for a 2 hour period during which the acceptor circulation supplied all the gasifier reheating requirements.	Gas inlet to regenerator quench tower kept plugging Agglomerates in regenerator.	High level in gasifier K.O. pot shut down compressors.	Modified venturi on the inlet of the regenerator quench tower.
10B	5/23/73-6/4/73	193	109	9	Husky Char	1,500	Achieve integrated Pilot Plant operation.	Achieved fully integrated plant operation for 9 hours without the need to inject air into the gasifier to maintain the char bed temperature. Obtained first quasi-stable heat and material balance data. Circulated calcined acceptor for 5 days without difficulty.	Differential pressure taps in regenerator and gasifier beds continued to plug. Sheared several pins in fresh dolomite feeders.	Spent dolomite transfer line plugged between gasifier boot and engager pot.	Revised operating procedures for filling fresh dolomite lockhoppers. Enlarged diameter of fuel char standleg from 2 inches to 3 inches.

Table 5-1. RUN HISTORIES (continued)

5

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
11A	6/15/73-6/21/73	115	15	0	Husky Char	0	Achieve stable steady-state operation for which heat and material balances can be calculated.	The run objectives were not accomplished due to the premature run termination.	Plugging of venturi upstream of regenerator quench tower resulted in pressure upsets which caused steam backflushing up the calcined acceptor standleg.	Calcined acceptor standleg plugged.	
11B	6/27/73-7/10/73	123	5	0	Husky Char	1,000	Achieve stable steady-state operation for which heat and material balances can be calculated.	The run objectives were not accomplished due to the premature run termination.	Sulfur corrosion in gasifier boot heater. Continued plugging of venturi upstream of regenerator quench tower. Ten minute power failure.	Calcined acceptor standleg plugged.	Regenerator quench tower venturi was installed in a vertical position with rodout device downstream.
12A	8/4/73-8/8/73	114	12	0	Husky Char	1,200	Determine individual heat losses from the regenerator and gasifier reactors, achieve integrated pilot plant operation and obtain steady-state balance period.	Successfully batch calcined regenerator acceptor inventory.	Plugging of calcined acceptor standleg, agglomerates in regenerator.	Transformer in motor control center failure causing recycle gas compressors to shut down.	Installed purge in calcined acceptor standleg.

6

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
12B	8/15/73- 8/23/73	140	11	0	Husky Char	1,000	Determine individual heat losses from the regenerator and gasifier reactors, achieve integrated pilot plant operation and obtain steady-state balance period.	Successfully batch calcined regenerator acceptor, obtained vessel heat loss data for both reactors.	Plugging of calcined acceptor standleg, agglomerates in regenerator.	Calcined acceptor standleg plugged.	Added second purge to calcined acceptor standleg.
12C	8/31/73- 9/5/73	126	15	0	Husky Char	1,200	Batch calcine regenerator acceptor bed and then commence acceptor circulation. Obtain steady-state integrated pilot plant operation.	Batch calcined acceptor inventory but steady-state operation not achieved. Due to the high acceptor attrition rate, balls of acceptor fines formed in the regenerator inventory.	Plugging of differential pressure taps and calcined acceptor standleg.	Acceptor lift line to regenerator plugged.	
12D	9/13/73- 9/19/73	110	17	0	Husky Char	1,000	Batch calcine regenerator acceptor bed and then commence acceptor circulation. Obtain steady-state integrated pilot plant operation.	Batch calcined acceptor inventory but steady-state operation not achieved. Due to the high acceptor attrition rate, balls of acceptor fines formed in the regenerator inventory.	Plugging of gasifier boot inlet gas line, continued to find agglomerates in the regenerator.	Calcined acceptor standleg plugged.	Revised operating procedure: (1) Continue circulating acceptor during calcining period. (2) Cool regenerator to 1600°F in the event that acceptor circulation is lost. (3) Limit gasifier boot heater to a maximum of 1500°F. Installed "Jim Dandy" mixer(a mechanical gas-solids-liquid mixing device) at regenerator quench tower inlet.

7

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
13A	9/28/73- 10/3/73	104	8	0	Husky Char	500	Determine if regenerator deposits experienced during Run 12 could be minimized by change in start-up procedures and obtain steady-state integrated plant operation.	Successfully calcined regenerator inventory while circulating acceptor. Unable to achieve desired steady-state operation.	Sulfur corrosion in gasifier boot heater. Plugging of "Jim Dandy" mixer, had to use parallel venturi.	Iron-nickel sulfide corrosion product plugged recycle gas line to gasifier boot.	
13B	10/6/73- 10/9/73	74	2	0	Husky Char	0	Determine if regenerator deposits experienced during Run 12 could be minimized by change in start-up procedures and obtain steady-state integrated plant operation.	Successfully calcined regenerator inventory while circulating acceptor. Unable to achieve desired steady-state operation.	Sulfur corrosion in gasifier heater and plugging of "Jim Dandy" mixer.	Iron-nickel sulfide corrosion product plugged again recycle gas line to gasifier boot.	Changed operating procedure: (1) Natural gas will be used to calcine initial acceptor inventory. (2) CO and H_2 in regenerator recycle will be limited to a maximum of 5%. (3) Gasifier boot heater outlet temperature limited to a maximum of 600°F.

Table 5-1. RUN HISTORIES (continued)

8

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
14A	10/25/73-10/30/73	128	30	0	Husky Char	0	Obtain steady-state integrated pilot plant operation period for which heat and material balances can be calculated.	Successfully calcined regenerator inventory using natural gas as fuel and minimized regenerator deposits. Successfully circulated calcined acceptor for 20 hours. The initially soft calcined acceptor became hard after several calcination-recarbonation cycles.	"Jim Dandy" mixer continued to plug. Gasifier boot recycle gas heater partially plugged. Tube ruptured in gasifier side flow heater during first startup. Char grinding was unreliable.	Plug in char transfer line from gasifier to regenerator.	
14B	11/7/73-11/9/73	53	0	0	Husky Char	0	Obtain steady-state integrated pilot plant operation period for which heat and material balances can be calculated.	Objectives not met due to early run termination.		Tube ruptured in regenerator air heater.	Replaced coils in gasifier boot heater. Installed zinc oxide sulfur removal system. Changed operating procedure to start up with dead-burned dolomite as a means of controlling agglomeration in regenerator. Replaced coil in regenerator air heater with coil from devolatilizer boot heater.

Table 5-1. RUN HISTORIES (continued)

9

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
15A	12/15/73- 12/29/73	324	4	0	Husky Char	800	Operate gasifier reactor only (no acceptor circulation) and establish a base set of operating conditions using Husky char as feedstock. Base conditions will be used to compare Husky char with Velva lignite. Test operation of ZnO unit for removing sulfur from the gasifier recycle gas.	Sulfur attack in gasifier recycle gas heaters was eliminated due to the successful operation of a new ZnO sulfur removal system. Obtained balance period for gasifier operation using Husky Char for feedstock.	No problems encountered.	No shutdown.	
15B	12/29/73- 12/30/73	48	10	0	Preoxidized Velva Lignite	1,000	Obtain balance period using Velva lignite with 5 percent preoxidation.	Obtained stable balance period using preoxidized Velva lignite.	No problems encountered.	No shutdown.	

Table 5-1. RUN HISTORIES (continued)

10

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
15C	12/30/73-1/1/74	48	18	0	Raw Velva Lignite	1,300	Determine if non-preoxided raw Velva lignite is a suitable gasifier feedstock.	Obtained stable balance period using raw (preoxidization not required) Velva lignite as feedstock. No operating problems experienced. Determined that gasifier operating conditions were sufficient to insure that all volatile materials in the lignite are cracked to methane, hydrogen and carbon oxides and that no tars or oils are produced.	No problems encountered.	Scheduled shutdown, gasifier operation only.	
16	1/14/74-1/23/74	196	124	8	Husky Char	1,200	Test new start-up procedure using dead-burned dolomite for the initial regenerator inventory.	New start-up procedure successfully reduced regenerator deposits and calcined acceptor bed fines. Successfully maintained integrated plant operation with acceptor circulation for 125 hours. Acceptor circulation supplied gasifier heating requirements for over 8 hours. Obtained 4 hour steady-state balance period.	"Jim Dandy" mixer plugged. Erosion of acceptor engager pot internals.	Hot spot on acceptor lift line.	Modified acceptor engager pot and lift line.

Table 5-1. RUN HISTORIES (continued)

11

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
17A	2/22/74-3/2/74	202	56	0	Husky Char	1,300	Achieve long-term stable integrated plant operation.	The failure of the B-201-IIIA gasifier recycle heater prevented obtaining objectives. The run provided the second successful demonstration of the new start-up procedure tested in Run 16.	Continued plugging of "Jim Dandy" gas mixer.	Gasifier recyle gas heater convection tube ruptured.	Increased diameter of "Jim Dandy" mixer from 3 inches to 4 inches.
17B	3/19/74-4/2/74	324	158	16	Husky Char	1,200	Achieve long-term stable integrated plant operation.	Achieved 158 hours of integrated plant operation, 72 hours of fresh acceptor make up and 16 hours of gasifier operation during which the circulating acceptor supplied the gasifier heat requirements. First time gasifier char bed temperature maintained at the 1500-1520°F level without the use of air injection.	Continued plugging of "Jim Dandy" mixer.	Operator error depressured system.	Removed "Jim Dandy" mixer and installed second venturi in parallel with existing venturi.

Table 5-1. RUN HISTORIES (continued)

12

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
18	4/19/74-4/29/74	234	156	14	Husky Char	1,300	Achieve long-term integrated plant operation.	The run ended before truly steady-state operating conditions could be achieved. Demonstrated that steam addition to the recycle gas flow used to fluidize the boot acceptor would eliminate the carborization attack of the boot recycle gas heaters.	Plugging of gasifier quench system.	Acceptor lift gas heater tube ruptured.	Changed operating procedure, put steam in gasifier boot heater as a means of controlling heater tube corrosion.
19	6/5/74-7/17/74	517	203	9	Velva Lignite	1,850	Achieve long-term integrated plant operation.	Demonstrated that raw lignite could be used as a gasifier feedstock with the plant operating in a totally integrated manner. Fed Velva lignite to the gasifier for 150 hours. Heat and material balance data obtained for 3 sets of operating conditions.	Leaks in expansion joints, Problems in lignite grinding section, electrical failures and leaks.	Leak at expansion joint on gasifier side flow line.	Installed second acceptor make-up lockhopper in series with first.

13

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
20	8/2/74-8/19/74	228	87	38	Velva Lignite	2,300	Achieve long-term integrated plant operation.	Successfully supplied all gasifier heat requirements with acceptor circulation for a total of 38 hours.	No serious problems encountered.	Gasifier internal cyclone fell.	No changes made. Repairs to cyclone made.
21	8/30/74-9/15/74	355	251	171	Velva Lignite	2,500	Maintain extended steady-state operation.	Achieved 251 hours of integrated plant operation; high acceptor activity achieved; produced synthesis gas that did not require shift conversion before methanation. Acceptor provided gasifier heat requirements for 171 hours.	Leaks in expansion joints due to chloride attack.	Acceptor interface lost due to build-up of intermediate fines.	Installed gasifier char removal system. Ordered new expansion joints made of Incoloy 825.
22A	9/20/74-9/27/74	120	20	0	Velva Lignite	2,500	Achieve long-term integrated plant operation.	Demonstrated use of 100% steam for boot acceptor fluidization.	Leaks in expansion joints again.	Lost interface due to deposit in gasifier boot, too rapid exchange of steam for recycle.	Replaced refractory in regenerator. Increased diameter of calcined acceptor standleg from 4 inches to 6 inches. Installed new bubble cap distributor in boot.

14

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
22B	11/22/74- 11/30/74	160	20	0	Velva Lignite	1,600	Achieve long-term integrated plant operation.	First operation of char removal system; new gasifier boot gas distributor performed well.	Gasifier quench tower level control froze.	Leak in expansion joint bellows.	Replaced all expansion joint bellows with new bellows made of Incoloy 825 which is less susceptible to chloride attack.
22C	12/13/74- 12/22/74	174	64	7.5	Velva Lignite	2,000	Achieve long-term integrated plant operation.	Obtained extensive data for correlating lift line pressure drop with acceptor circulation rate.	No major problems occurred.	Low boot flow apparently caused stratification of solids in boot which in turn plugged acceptor lift line.	Changed operating procedure, set minimum on boot flow.
23	1/7/75- 2/5/75	577	223	97	Velva Lignite	2,700	Achieve extended operation with 100% steam to boot.	Higher boot gas velocities used successfully to improve interface control, smooth operation with 70-75% steam in boot. Char removal system was used to effectively control the build up of intermediate fines. Source of intermediate fines material determined.	Breakdowns in the lignite grinding section caused two delays during the run.	Hot spot on acceptor lift line.	Replaced lift line slip joint section, found errosion was due to misalignment.

Table 5-1. RUN HISTORIES (continued)

15

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
24	2/21/75-3/14/75	286	150	0	Velva Lignite	2,800	Extended operation with 100% steam to boot.	Methodical removal of air and recycle gas from gasifier resulted in smoothest plant operation to date; char removal system successfully used in removing intermediate fines from gasifier.	Restriction in regenerator recycle gas heater.	Plug at inlet of gasifier quench tower.	Installed venturi scrubber and revised gasifier quench tower inlet.
25	3/31/75-4/10/75	327	121	0	Velva Lignite	3,000	Achieve extended operation with 100% steam to boot.	Accomplishment of Run 24 repeated.	Plugging of gasifier quench venturi, loss of regenerator fuel char feed resulting from pressure upsets caused by switching char removal hoppers.	Pressure upset caused by switching char removal hoppers defluidized gasifier bed and caused acceptor to agglomerate in the transition section of the gasifier.	Revised gasifier venturi, change of char withdrawal hoppers from parallel to series. Installed auxiliary char feed system to regenerator.

Table 5-1. RUN HISTORIES (continued)

16

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
26A	5/16/75-5/22/75	246	126	0	Velva Lignite	2,700	Achieve extended operation with 100% steam to boot.	Newly installed auxiliary char fuel system added flexibility to regenerator and char transfer operation; modified (parallel lock-hoppers) char removal system operated successfully; new differential pressure control system on char standleg sloped section prevented fines plugging in standleg.	High dP on lignite grinding system bag house severely limited grinding capacity, continued plugging of gasifier quench system venturi.	Inability to transfer dolomite from gasifier to regenerator, caused by the calcined dolomite transfer line extension inside the regenerator falling off and lodging in the bottom of the regenerator.	Replaced dust bags in 100 area bag house, replaced extension of calcined acceptor return line, installed rod-outs in gasifier quench system venturi.
26B	6/6/75-6/16/75	237	132	64	Velva Lignite	2,400	Achieve extended operation with 100% steam to boot. Improvement of char transfer control and operation.	High acceptor activity (0.4) obtained; data for study on char transfer system pressure balance obtained; char removal system control of gasifier intermediate fines confirmed.	Continued plugging of gasifier quench venturi, fortunately, rod devices prevented the pressure drop from becoming excessive. Restriction of dP tap in gasifier boot caused acceptor level to build up into the transition section.	A power failure caused the regenerator bed to defluidize and the engager pot at the bottom of the acceptor lift line to plug.	Revised control of gasifier boot interface level.

Table 5-1. RUN HISTORIES (continued)

17

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
27A	6/27/75-7/7/75	210	54	0	Velva Lignite	2,400	Achieve extended operation with 100% steam to boot; obtain balance periods to study effects of process variables.	Premature shutdown precluded any significant results.	No problems encountered.	Power failure shut down compressors which in turn defluidized gasifier and regenerator beds resulting in a plugged engager pot below the regenerator.	Installed a time delay system to automatically close all solids valves after a power failure of two seconds or greater duration. Installed sample tap in transition of gasifier. Revised gasifier interface control.
27B	7/15/75-7/22/75	126	16	0	Velva Lignite	2,100	Achieve extended operation with 100% steam to boot; obtain balance periods to study effects of process variables.	Premature shutdown precluded any significant results.	High dP on lignite grinding system bag house. Experienced afterburning in regenerator.	Regenerator bed became defluidized and acceptor lift line plugged while reducing gas velocity in an attempt to eliminate afterburning.	No major revisions.
27C	7/25/75-8/11/75	408	243	65	Velva Lignite	2,500	Achieve extended operation with 100% steam to boot; obtain balance periods to study effects of process variables.	100% steam to boot attained for 25 hours before non-process problem forced shutdown; char removal system controlled gasifier intermediate fines over extended (10 day) run period.	Experienced upsets due to operation of char withdrawal system. Accidental boiler shutdown.	Loss of regenerator fuel char control due to weld failure on LCV-2002 butterfly.	Revised operating procedure for char withdrawal system. Removed primary steam orifices and shipped to testing laboratory for calibration. Switched to Minnekahta limestone acceptor.

Table 5-1. RUN HISTORIES (continued)

18

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
28A	8/26/75- 9/1/75	134	64	0	Velva Lignite	2,200	Demonstrate plant operability with the new Minnekahta limestone and with 100% steam to boot; obtain balance period data.	Minnekahta limestone used successfully in plant with Velva lignite feedstock.	No problems encountered.	Gasifier boot became defluidized when a portion of the fluidizing steam apparently by-passed the boot through the spent acceptor lockhopper.	Installed more sensitive instrumentation to detect condition of spent acceptor lockhopper operation.
28B	9/12/75- 9/27/75	360	293	236	Velva Lignite	2,250	Demonstrate plant operability with the new Minnekahta limestone and with 100% steam to boot; obtain extended balance period data.	Limestone used successfully with 85 hours of 100% steam in boot; 12 day plant operation; two balance periods of 33 and 40 hours obtained.	Momentary bridging of the acceptor in the gasifier boot at the point where the lower acceptor standleg, CD-204, enters the boot caused the acceptor withdrawal from the boot to become erratic at times.	Upset was apparently triggered by a plug in the lower acceptor standleg sample tap and purge tap. Subsequently, the acceptor standleg opening in the gasifier boot began to bridge again, ultimately resulting in a plug in the upper section of the standleg which could not be dislodged.	Increased the diameter of the lower acceptor standleg from 4 inches to 6 inches. Changed lower acceptor standleg and char standleg purges from 200 PSIG recycle gas to 300 PSIG inert gas.

Table 5-1. RUN HISTORIES (continued)

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
29A	10/16/75- 10/25/75	159	27	0	Velva Lignite	2,250	Operate plant at steady-state for seven days with no air in the gasifier; operate methanation unit for first time.	Premature shutdown precluded any significant results.	Loss of regenerator fuel char due to plugged tap on lignite lockhopper dP pressure controller.	Ruptured coil in B-205 (regenerator lift gas) heater.	Installed new Incoloy 800 coil in B-205 heater. Increased the length of the dip tube in F-222 (acceptor engager pot) by 5 inches.
29B	11/7/75- 11/17/75	244	109	52	Velva Lignite	2,275	Operate plant at steady-state for seven days with no air in the gasifier; operate methanation unit for first time.	Methanation unit brought onstream for first time and operated successfully for 48 hours.	Operation of the reject acceptor lockhopper and the char removal lockhopper occasionally upset plant operation.	The purged acceptor withdrawal line became plugged. A high differential pressure across the gasifier boot distributor developed while attempting to unplug this line which prompted the decision to terminate the run.	Installed blinds in lines to isolate the regenerator from the gasifier for Run 30.
30	11/27/75- 12/7/75	232	188	0	Husky Char	325, 388, 428	Obtain heat and material balance data for an isolated regenerator so the vessel heat losses can again be determined; test operation of the Elliot turbine blade test unit.	Three data balance periods were obtained; the turbine test unit was successfully operated for 127 hours without problems.	No problems encountered.	Scheduled shutdown, regenerator operation only.	Installed external cyclone on gasifier overhead gas line.

20

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
31	12/9/75-12/28/75	469	352	0	(1)Ilusky Char (2)Pre-oxidized Westmoreland Sarpy Creek Subbituminous (3)Non-pre-oxidized Westmoreland Sarpy Creek Subbituminous Coal (4)Non-preoxidized Wyodak Subbituminous Coal	(1)1,275 (2)1,530 (3)1,575 (4)1,575	By operating the gasifier as an isolated vessel, test suitability of using subbituminous coals for process feedstock.	Three subbituminous coals were tested and determined to be suitable gasifier feedstock; preoxidation of the coal was determined to be unnecessary; coal feeders were calibrated at operating conditions.	No problems encountered.	Scheduled shutdown, gasifier operation only.	None
32	1/3/76-1/13/76	224	59	0	Glenharold Lignite	1,470	Determine suitability of using medium sodium content Glenharold lignite as gasifier feedstock (isolated gasifier operation). (Approximately 1 week of steady-state operation.)	The run results indicated that Glenharold lignite would be a suitable feedstock.	Gasifier operation only. Sub-zero weather caused a three day curtailment of natural gas.	Hot spots in the gasifier bed developed when steam flow was reduced in an effort to inhibit kinetics.	Moved reject acceptor withdrawal point from the bottom of the gasifier boot to a side nozzle on the regenerator. Increased the diameter of the upper sloped section of the regenerator fuel char standleg from 5 inches to 4 inches. Replaced metal cone sections of the slip joints on the acceptor lift line (CD-209) with ceramic cone

21

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
32 Cont.											sections. Replaced cracked cast iron base of 100 area roller mill with a steel base.
33A	1/23/76-1/30/76	174	67	10	Velva Lignite	2,100	Technical feasability of the process is to be proven, using Velva lignite; methanation unit is to produce synthetic natural gas.	Premature shutdown precluded any significant results.	None	Gasifier boot heater went down and could not be immediately restarted. During this period the gasifier boot gas cooled and the boot became defluidized which caused a plug near the spent acceptor outlet line.	None.
33B	2/5/76-2/22/76	416	291	249	Velva Lignite	2,700	Technical feasability of the process is to be proven, using Velva lignite; methanation unit is to produce synthetic natural gas.	Technical feasability of process proven: over 8 days operation producing synthetic natural gas, with all gasifier heat duty supplied by circulating acceptor, 100% steam to boot, and 6 day steady-state balance period; new F-228 lockhopper system operated successfully to reliably remove spent acceptor and control intermediate fines level.	Valves below F-204B, lignite lockhopper developed a leak which interrupted lignite feed.	Mechanical failure of calcined acceptor standleg prevented transfer of calcined acceptor from the regenerator to the gasifier.	Installed a shorter nozzle on the calcined acceptor standleg (CD-206). New nozzle does not extend into the regenerator bed. Installed a new coil in B-201-IIA, gasifier boot heater.

22

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
34A	3/17/76-3/22/76	108	13	0	Glenharold Lignite	2,300	Demonstrate plant operation using high sodium content Glenharold lignite; operation of methanation unit.	Premature shutdown precluded any significant results.	None	A hot spot developed on the acceptor lift line, CD-208. The hot spot was found to be caused by an insulation void.	Repaired hot spot on acceptor lift line. Replaced gas distributor ring and connecting line in regenerator.
34B	3/26/76-4/1/76	144	51	14	Glenharold Lignite	2,300	Demonstrate plant operation using high sodium content Glenharold lignite; operation of methanation unit.	Premature shutdown precluded any significant results.	Transfer was blocked by a plug in the lower acceptor standleg and was cleared. The regenerator acceptor and spent acceptor sample stations were both unplugged. Plugging problems were encountered in the ground coal scalping screen oversize line. Acceptor transfer from the boot was reduced due to upset in the boot.	An upset occurred in the boot resulting in loss of acceptor transfer from the boot. Transfer could not be regained.	After more than three years of service, replaced cone bottom of regenerator external cyclone due to metal erosion. Installed a new K.O. pot on the suction line to gasifier recycle compressors. Installed a level probe in the lower acceptor feed lockhopper.

Table 5-1. RUN HISTORIES (continued)

23

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
35	4/13/76-4/25/76	281	176	25	Glenharold Lignite	2,270	Demonstrate plant operation using high sodium content Glenharold lignite; operation of methanation unit.	Despite 103 hours of lignite feed, the run did not conclusively demonstrate that the process is tolerant of high sodium coals.	The run was continually plagued by higher than normal gasifier bed densities. Reliable fuel char transfer was gained after a system leak was repaired at a thermocouple fitting in the char line. Sheared a pin on the acceptor feeder. Restricted taps caused upsets in the boot and char transfer lines. A minor unexplained upset occurred in the boot and was overcome. Char transfer was lost four times due to malfunction in the char removal system.	Acceptor transfer from the boot was lost and could not be regained.	None
36	5/6/76-5/13/76	169	83	52	(1) Velva Lignite (2)Glenharold Lignite	(1)2,130 (2)2,760	Demonstrate new start-up procedure for use with Glenharold lignite; attain two day balance period operation.	Start-up procedure (using Velva lignite when air is still in gasifier) proved successful in eliminating gasifier ash deposits.	Lignite screw conveyor had a loose bearing. Sticking level switch on lignite surge bin. Coal scalping screen oversize line plugged continually. Sudden decrease	Acceptor transfer from the boot was lost and could not be regained.	New air distributor ring was installed in the regenerator.

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
36 cont.									in acceptor transfer due to refractory entering the calcined acceptor standleg. Suffered 8 power outages due to high winds.		
37A	5/21/76-5/27/76	135	50	19	Rosebud Subbituminous	2,125	Demonstrate plant operation using Rosebud subbituminous coal feedstock; attain extended balance period operation.	Plant operation proceeded smoothly with Rosebud coal feed for 39 hours, demonstrating plant operability with Rosebud subbituminous coal.	Rosebud coal was very wet and difficult to grind, high dP on lignite grinding system bag house.	Apparent plug in gasifier transition section due to the high fines content of the coal feedstock caused loss of acceptor transfer and could not be regained.	No major revisions.
37B	6/5/76-6/14/76	195	130	68	Rosebud Subbituminous	2,125	Demonstrate plant operation using Rosebud subbituminous coal feedstock; attain extended balance period operation.	Demonstrated smooth plant operation with Rosebud coal feed for 113 hours; 100% steam to gasifier boot for 33 hours. Determined that coal feedstock had been contaminated with ash slag at power plant storage pile.	High dP on lignite grinding system bag house. Gasifier side flow heater coil failed due to apparent localized overheating or creep.	Sustained power failure due to high winds and rain.	Installed old devolatilizer cyclone in gasifier. Modify regenerator ash removal system to dump to tote bin in place of slurry.

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
38A	7/5/76-7/10/76	188	92	0.5	Wyodak Subbituminous	2,160	Demonstrate technical feasibility of process using Wyodak subbituminous coal feedstock.	Process operating conditions maintained for 92 hours, air removed from gasifier, 88% of dead-burned dolomite inventory changed out, Wyodak coal fed for 88 hours.	Chain broke in the lignite elevator. Tore hole in the dolomite scalping screen. The recarbonated acceptor sample station was plugged during the run.	The level control valve on the interface level reached over capacity for a short duration causing the interface to rise into the transition section. A bridge then formed in the transition section causing loss of acceptor transfer from the boot which could not be regained.	Enlarged interface level control valve from four inches to five inches. Enlarged nozzle in engager pot to six inches.
38B	7/20/76-7/21/76	152	65	11	Wyodak Subbituminous	2,150	Demonstrate technical feasibility of process using Wyodak subbituminous coal feedstock.	Run progressed to similar state as in 38A.	Oversized char hindered the ability to set the char interface and also establish char transfer.	Several large pieces of agglomerated acceptor entered the lower acceptor standleg and lodged on the valve causing loss of transfer from the boot which could not be regained.	None

Table 5-1. RUN HISTORIES (continued)

26

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
38C	7/31/76- 8/28/76	375	236	0	Wyodak Subbitu- minous	2,530	Demonstrate technical feasibility of process using Wyodak sub- bituminous coal feedstock.	Planned and volun- tary shutdown pro- ceeded smoothly; brief balance per- iod was obtained; the circulation rate of aged acceptor was directly measu- red.	A leak was discov- ered in the regene- rator overhead line and was re- paired. A deposit of char in the lower CD-204 spool piece burned and heated the pressure shell to over 400°F. A large piece of refractory blocked the acceptor lift line in the regene- rator causing a flow reversal in the lift gas. The line to the spent acceptor lock- hopper was plugged and had to be cleared. Could not immediately initiate char transfer through the char lift line due to a plug which was removed. Problems with bag house caused plant to go on hold con- ditions twice. A restriction in the lower acceptor stand- leg caused the inter- face to rise into the transition section.	Planned shutdown.	A manual shutoff valve was installed in the char stand- leg. Installed a new char screw con- veyor to transfer char from storage to Redler con- veyor.

Table 5-1. RUN HISTORIES (continued)

27

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
38C cont.									Interface had to be blown away. The interface was easily recovered. The auxiliary fuel char contained a large amount of clay.		
39	9/17/76-10/4/76	371	192	162	Glenharold Lignite	2,560	Demonstrate plant operation with medium-to-high sodium content Glenharold lignite; evaluate operation with reduced steam partial pressure in the gasifier boot.	Plant operability with medium-to-high sodium content lignite was clearly demonstrated; reduced steam partial pressures in the boot and eliminated boot acceptor deposits; gasifier char bed density was controlled by new procedures; methanation unit was operated for two days.	The recarbonated acceptor control valve had to be removed and repaired. Plant put on hold due to loss of city water supply. The regenerator cyclone developed leaks. Pressure taps plugged sending false signals which drained the boot. Brief boiler shutdown caused loss of steam flow.	The secondary regenerator cyclone developed leak due to erosion which was too severe to repair while operating the plant. Shutdown was orderly.	The char removal system was removed from the system. CO_2 addition changed from side flow to boot flow.
40A	10/22/76-10/28/76	138	65	0	Texas Lignite	2,440	Demonstrate plant operation with Texas lignite feedstock.	Plant operated for 55 hours with Texas lignite feed.	None	A loss of power caused the regenerator bed to slump. The bed could not be refluidized.	None

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
40B	11/10/76- 11/21/76	292	194	0	Texas Lignite	2,550	Achieve steady-state plant operation with Texas lignite feedstock and air injection to the gasifier; test use of Velva lignite as auxiliary fuel to the regenerator.	Plant operated successfully at specified conditions with Texas lignite feedstock; two balance periods were obtained; Velva lignite proved acceptable as auxiliary fuel.	The main air compressor had to be shut down once to repair the rings and once to replace the brushes in the electric motor. Instrument lines froze on several occasions.	The dip tube of the internal gasifier cyclone fell off and lodged in the boot causing the gas to travel up the tube in place of the bed.	The new refractory acceptor lift line and a new ring type boot distributor were installed.
41A	12/10/76- 12/18/76	153	31	0	Wyodak Subbituminous	2,160	Demonstrate technical feasibility of process using Wyodak subbituminous coal; test the new refractory-lined acceptor lift line; test use of Wyodak subbituminous coal as auxiliary fuel to the regenerator.	No problems were experienced with operation of the new acceptor lift line; an inspection of the line after the run revealed the line to be in excellent condition; Wyodak subbituminous coal proved acceptable as auxiliary fuel.	None	Transfer through the recarbonated acceptor control valve was lost and could not be regained. Inspection showed that a small amount of dead-burned dolomite which agglomerated in a dead area under the boot distributor became dislodged and blocked the entrance to the standleg.	The dead area under the boot distributor was filled in with refractory.

Table 5-1. RUN HISTORIES (continued)

29

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
41B	12/22/76- 12/29/76	133	71	36	Wyodak Subbituminous	2,250	Demonstrate technical feasibility of process using Wyodak subbituminous coal; test the new refractory-lined acceptor lift line; test use of Wyodak subbituminous coal as auxiliary fuel to the regenerator.	Again, acceptor lift line was in excellent condition after the run and Wyodak subbituminous coal operated successfully as auxiliary fuel.	None	The run ended during attempts to regain the interface after it had been purposely destroyed. The interface was destroyed due to its instability resulting from a low acceptor particle density.	The regenerator internal diameter was reduced from 33 inches to 24 inches. Installed air nozzle in regenerator for future use.
42	1/29/77- 2/13/77	296	174	146	Velva Lignite	2,350	Operate regenerator using only air for acceptor fluidization (no recycle gas, in the acceptor lift line); demonstrate regenerator operation with a 24-inch inside diameter and 1-3% CO in regenerator overhead gas.	Demonstrated use of 100% air in acceptor lift line. Demonstrated regenerator operation using air alone to fluidize acceptor inventory. Two steady-state balance periods were obtained; the reduced diameter regenerator operated well; no deposits were formed under the reducing atmosphere.	Cold weather caused some instrument lines to freeze. One upset resulted from a sudden loss of boot flow. The interface was destroyed and regained and the unit lined out. Another upset occurred when the regenerator vent valve plugged. Trouble was experienced with regenerator quench tower	Planned shutdown.	Replaced B-205 heater coil. Coil had deteriorated due to stress corrosion caused by sulfur attack.

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
42 cont.									plugging due to sudden carryover.		
43A	3/1/77-3/11/77	192	127	53	Velva Lignite	2,380	Operation of the regenerator was to be assessed under oxidizing, neutral, and reducing conditions; exclusive use of air in the regenerator and in the acceptor lift line was to be tested further.	The acceptor lift line operated satisfactorily with 100% air; methanation unit was operated for 66 hours.	Run delayed due to bag house problems.	A four hour loss of electrical power.	The calcined acceptor standleg was replaced because of bends in the line. Enlarged calcined acceptor flow control valve from 4" to 5".
43B	3/28/77-4/10/77	282	115	66	Velva Lignite	2,200	Operation of the regenerator was to be assessed under oxidizing, neutral, and reducing conditions; exclusive use of air in the regenerator and in the acceptor lift line was to be tested further.	The acceptor lift line operated satisfactorily with 100% air; demonstrated regenerator operation using air alone to fluidize acceptor inventory.	The coal grinding area couldn't keep up with gasification area due to extremely wet coal.	A plug formed in the overhead transfer line between the gasifier and the acceptor flow control valve.	None.

31

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
44A	4/20/77- 4/30/77	220	114	96	Wyodak Subbitu- minous	2,000	Demonstrate technical feasibility of process using Wyodak subbituminous coal feedstock with Minne- kahta lime- stone acceptor; demonstrate regenerator operation under neutral and oxidizing conditions.	Stable 12 hours balance period obtained with 100% air to the regenerator and 100% steam to the gasifier.	The unit was de- pressured to re- move a plug in the char lift line. The unit was dumped and depressured to repair the in- let valve to re- ject acceptor hopper. Low acceptor parti- cle density.	The interface mixed in the boot due to low boot flow needed to keep char bed density down. The interface was blown away and could not be regained.	None.
44B	5/10/77- 5/16/77	146	83	66	Wyodak Subbitu- minous	2,100	Demonstrate technical feasibility of process using Wyodak subbituminous coal feedstock with Minne- kahta lime- stone acceptor; demonstrate regenerator operation under neutral and oxidizing conditions.	The run results demonstrated that Minnekahta lime- stone and Wyodak subbituminous coal cannot be used to- gether in the pilot plant due to the low accep- tor particle density which is obtained for this acceptor feedstock combination.	Low acceptor particle den- sity.	The interface was lost when acceptor quit falling into the boot causing the bed level to rise rapidly. The interface could not be regained.	None

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
45	5/25/77- 6/10/77	397	293	124	Wyodak Subbitu- minous	2,100	Demonstrate technical feasibility of process using Wyodak subbituminous coal feedstock with Tymochtee dolomite acceptor; operate the methanation unit at a higher pressure (280 PSIA); demonstrate regenerator operation under neutral and oxidizing conditions.	Plant operation with the subbituminous coal and the dolomite acceptor was a success and a planned, voluntary shutdown was executed; the methanation unit was successfully operated at 280 PSIA for the first time; the regenerator was successfully operated under neutral and oxidizing conditions for 8 and 30 hours, respectively.	Accumulation of intermediate fines in the gasifier. The fines appeared to originate from the acceptor.	Voluntary shutdown.	A CO_2 stripping section was installed in the upper end of the overhead acceptor transfer line. A new sample point was added to the overhead acceptor transfer line.
46A	6/30/77- 7/4/77	101	4	0	Velva Lignite	2,270	Investigate plant operation at a higher operating pressure (190 PSIG); determine the effects of higher steam partial pressure on acceptor activity; operate the single-tube methanation reactor.	Premature shutdown precluded any significant results.	Gasifier differential pressure tap broke giving erroneous values for the transition section dP.	Ruptured steam line downstream of B-207 steam superheater.	Repaired dP tap and ruptured steam line.

Table 5-1. RUN HISTORIES (continued)

33

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
46B	7/6/77- 7/15/77	164	58	27	Velva Lignite	2,600	Investigate plant operation at a higher operating pressure (190 PSIG); determine the effects of higher steam partial pressure on acceptor activity; operate the single-tube methanation reactor.	Premature shutdown precluded any significant results.	The grid which covers the inlet to the calcined acceptor standleg tore loose and wedged in TCV-2030. Calcined acceptor transfer then could not be stopped. Slip joints in the char lift line eroded.	Steam surges in boot caused loss of char-acceptor interface control.	Tuned boiler pressure controller. Replaced char lift line slip joints. Installed new gasifier boot steam distributor. Single tube methanator installation completed.
46C	7/29/77- 8/10/77	271	186	160	Velva Lignite	2,670	Investigate plant operation at a higher operating pressure (190 PSIG); determine the effects of higher steam partial pressure on acceptor activity; operate the single-tube methanation reactor.	Plant operation at 190 PSIG was demonstrated; two balance periods with high boot steam partial pressures (12.0 and 12.2 atmospheres) were obtained; both the multi- and single-tube methanation reactors operated successfully.	Well into the run, the air compressor had to be shut down for repairs. Lost all boot flow when back pressure control valve slammed shut. Lost boiler due to power dip.	Boot upset caused by sudden loss of recycle gas flow to boot during period when recycle gas was being changed out for steam.	Modified boot recycle control valve to improve control for low flow conditions.

Table 5-1. RUN HISTORIES (continued)

Run No.	Date	Hours At Pres.	Hours At Temp.	Hours Without Air In Gasifier	Feed Type	Feed Rate LB/HR	Purpose	Results and Accomplishments	Problems Encountered	Cause of Termination	Revisions Made Prior to Next Run
47A	9/1/77-9/8/77	168	113	86	Velva Lignite; Minnekahta Limestone/Reconstituted Acceptor	2,760	Assess the use of reconstituted limestone as a suitable acceptor for the process.	Reconstituted acceptor was demonstrated to be active enough to supply all gasifier heat requirements; gasifier char bed density was always under complete control; a 24 hour balance period was obtained.	Leak in gasifier external cyclone caused shutdown of initial start-up. Plugged sensing taps were common. The ZnO_2 towers filled with water and upset process flows to the gasifier and fresh acceptor feed line plugged several times when reconstituted acceptor fed.	A gasifier boot deposit fell into CD-204 recarbonated acceptor transfer line stopping acceptor circulation.	Skirting was added to the gasifier boot distributor ring to eliminate "dead spots" in the gasifier boot.
47B	9/24/77-10/1/77	152	120	101	Velva Lignite; Minnekahta Limestone/Reconstituted Acceptor	2,700	Assess the use of reconstituted limestone as a suitable acceptor for the process.	Again, reconstituted acceptor operated successfully in the pilot plant and the gasifier char bed density was under control; a 48 hour steady-state balance period was obtained; the methanation unit was operated with no recycle for the first time.	Uncontrolled char transfer and a plugged acceptor lift line each caused a shutdown before the run successfully began. Char transfer upsets and plugged sensing taps were common during the run.	A gasifier boot deposit fell into CD-204 recarbonated acceptor transfer line stopping acceptor circulation.	None (last run).

Table 5-1. RUN HISTORIES (continued)

35

5.2.1 FLUIDIZATION

The two-vessel operation of the CO_2 acceptor process employs three separate fluidized beds. These are : (1) the gasifier char bed, (2) the bed of accumulated spent acceptor in the gasifier boot, and (3) the regenerator acceptor bed. Each of these fluid beds must be controlled differently. The gasifier char bed must be expanded enough to allow the acceptor to shower through it to provide heat for the gasification reactions. The spent acceptor in the gasifier boot must be fluidized with a gas rate suffient to strip char from the showering acceptor but low enough to allow the acceptor to collect. Finally, the gas rate to the regenerator must be great enough to: (1) intimately mix fuel char with spent acceptor so that hot spots do not exist, and (2) strip the char ash from the bed. At the same time, fluidization of the char and regenerator beds must be gentle enough to avoid excessive particle attrition or carryover. Therefore, the fluidization characteristics of both char and acceptor must be thoroughly understood.

During the bench-scale studies, extensive data were obtained in batch fluidized systems having bed diameters of 1, 2, and 4 inches. Fluidized bed densities were determined by dividing the known weight of solids by the bed volume. The bed volume, in systems at ambient conditions, was defined as the product of the bed cross-sectional area and the average maximum fluidized bed height*. In many systems, the bed height fluctuates considerably due to formation and collapse of gas bubbles. The above definition of bed height was chosen to conform with the reality of containing a fluidized bed in a process vessel. Data also were obtained in systems operated at pressures of up to 20 atm abs and at temperatures up to $1500°F$. In these systems the vessels were equipped with internal overflow weirs. Visual studies at ambient conditions in the mock-ups of these vessels showed that the bed heights defined by the top of the internal weirs corresponded with the observed average maximum bed heights.

Using results of the bench scale studies and data available in the literature, a generalized correlation was developed to predict the fluidized bed density in any system.[1] After publication, the original correlation was modified to include data on new systems and to improve the accuracy of the predicted bed densities at high bed expansions. The revised correlation has not been published in the general literature, but will be presented in the future.

During pilot plant Run 5, fluidization tests in both the gasifier and regenerator showed that the measured bed densities, calculated from the pressure difference between two pressure taps immersed in the fluidized bed at known spacings, changed very little as the fluidizing velocity was varied over a wide range. Several pairs of taps were involved in the tests, including both vertical and side probes as discussed in Section 11.3. Impulse lines from the taps led to Foxboro   P trans-

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*Average maximum fluidized bed height is obtained by averaging the maximum heights of a surging bed over a period of 10 to 60 seconds.

(1) Phase II, "Bench-Scale Research on CGS Process-Studies on Mechanics of Fluo-Solids Systems," Jan. 1970, R & D Rpt. No. 16--Interim Rpt. No. 3, Book 1, NTIS: PB-184718/AS.

mitters which sent pneumatic signals to recorders. The surging fluidized beds required that the fluctuating static pressures at the taps be dampened. Snubbers installed either in the impulse lines or in the signal lines from the transmitter were satisfactory.

Figure 5-1 and 5-2 show some of the data obtained during fluidization tests in the gasifier and regenerator which were operated at process conditions. Predicted densities are those calculated from the revised correlation.

Further studies using a 12-inch diameter glass model equipped with a coaxial pair of pressure taps, which could be positioned accurately anywhere in the fluidized bed, confirmed the Run 5 implications that bed densities calculated from differential pressure measurments did not reflect the actual observed bed densities. Some typical data from the glass model are presented in Figures 5-3 and 5-4. System properties are shown in the figures. The measured bed densities are those calculated from differential pressure data. A manometer was used to determine differential pressure. Snubbing was accomplished by use of needle valves in the impulse lines. The observed bed densities correspond to the average maximum bed height and the known weight of solids in the bed.

The original correlation was intended to predict bed densities for highly expanded beds. Data for the correlation had been obtained for materials with narrow size fractions. A single average particle size was therefore used to represent the materials in the correlation. However, no single particle size can accurately represent the plant material, either char or acceptor, due to wide particle size distribution.

It was found that a summing procedure allowed contributions from each particle size to be accounted for. Mathematically, the procedure may be represented by:

$$\epsilon_{mix} = \sum_{i=1}^{n} \epsilon_i X_i \qquad (5-1)$$

where: Superficial gas velocity is constant and

$$0.47 \leq \epsilon \leq 1.0$$

n = number of size cuts

X = weight fraction of each size cut

ϵ = void fraction of each size cut

The revised correlation is used to calculate a void fraction for each particle size at a given gas velocity. If the gas velocity is less than that required for incipient fluidization of a particular particle size, a value of 0.47 is assigned for the void fraction. Similarily, a void fraction value of 1 is assigned for all particle sizes that have a terminal velocity which is less than the gas velocity. As more size fractions are used, accuracy is improved.
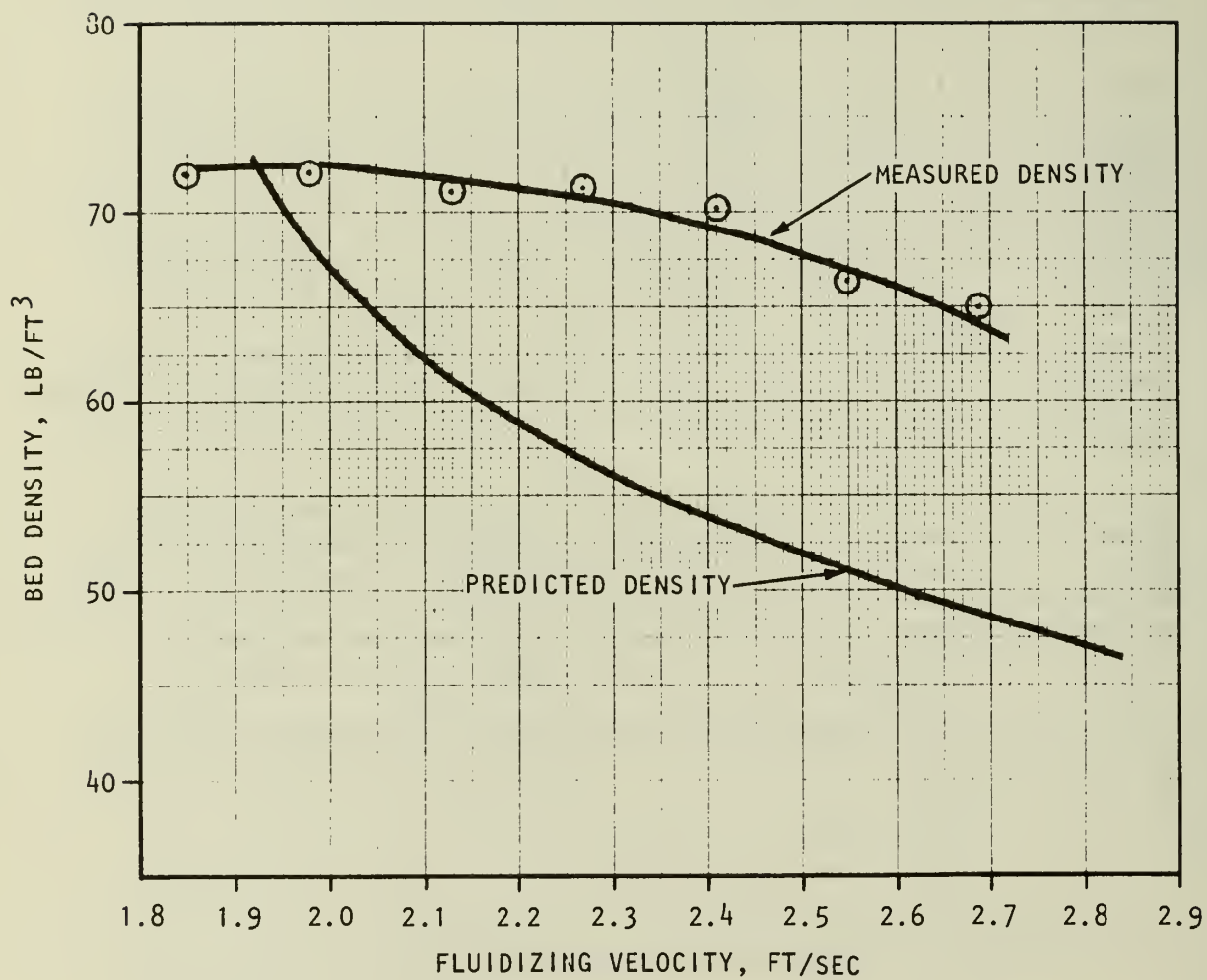
PRESSURE 150 PSIG

BED TEMP 1280°F

PARTICLE DENSITY 145 LB/FT^3

EFFECTIVE PARTICLE DIA .071 INCHES

FLUIDIZING GAS AIR

Figure 5-1. REGENERATOR FLUIDIZATION TEST, RUN 5, OCTOBER 17, 1972
DOLOMITE, 8 x 28 TYLER MESH
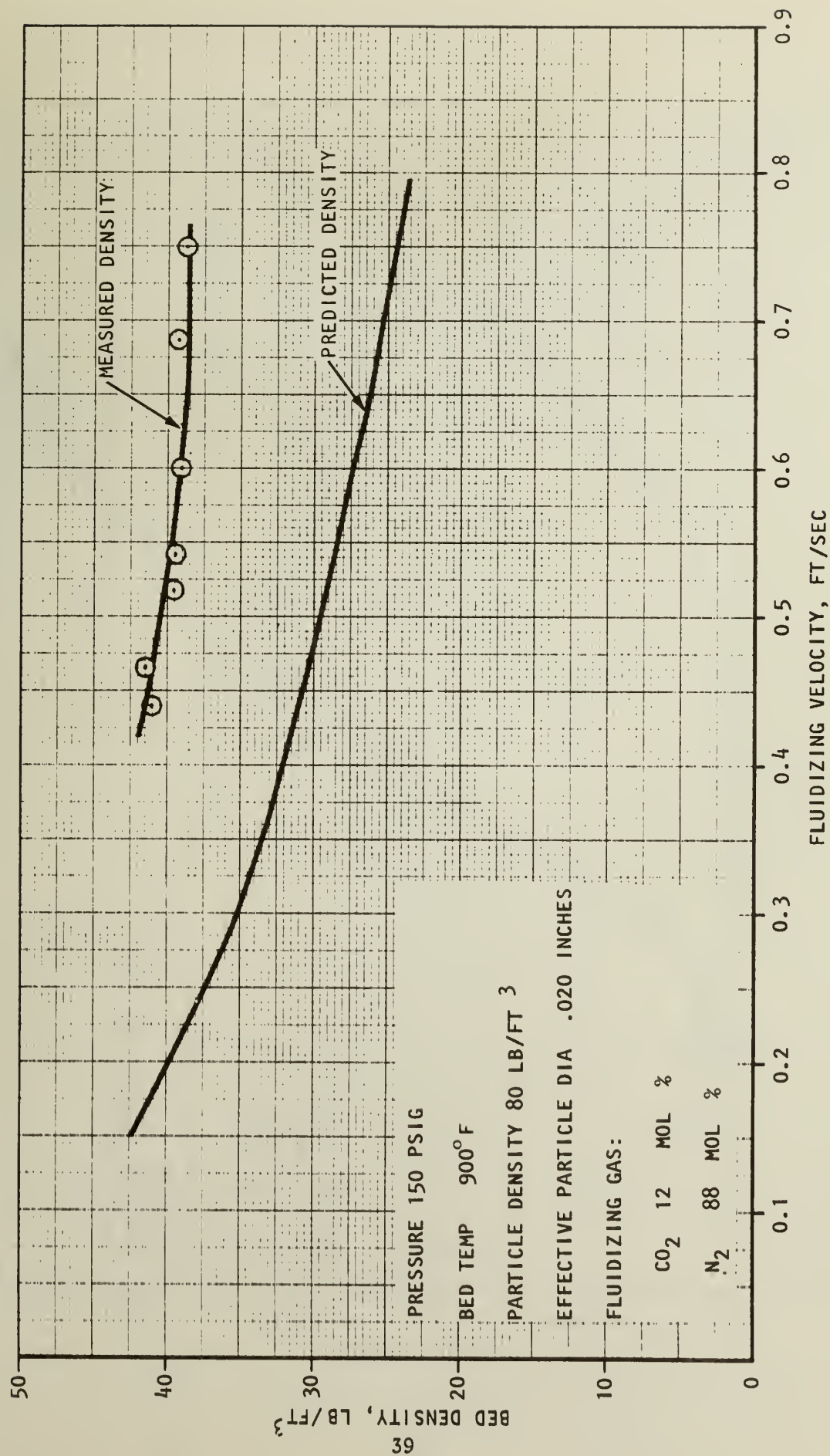
Figure 5-2. GASIFIER FLUIDIZATION TEST, RUN 6, JANUARY 25, 1973
CHAR, 14 x 100 TYLER MESH
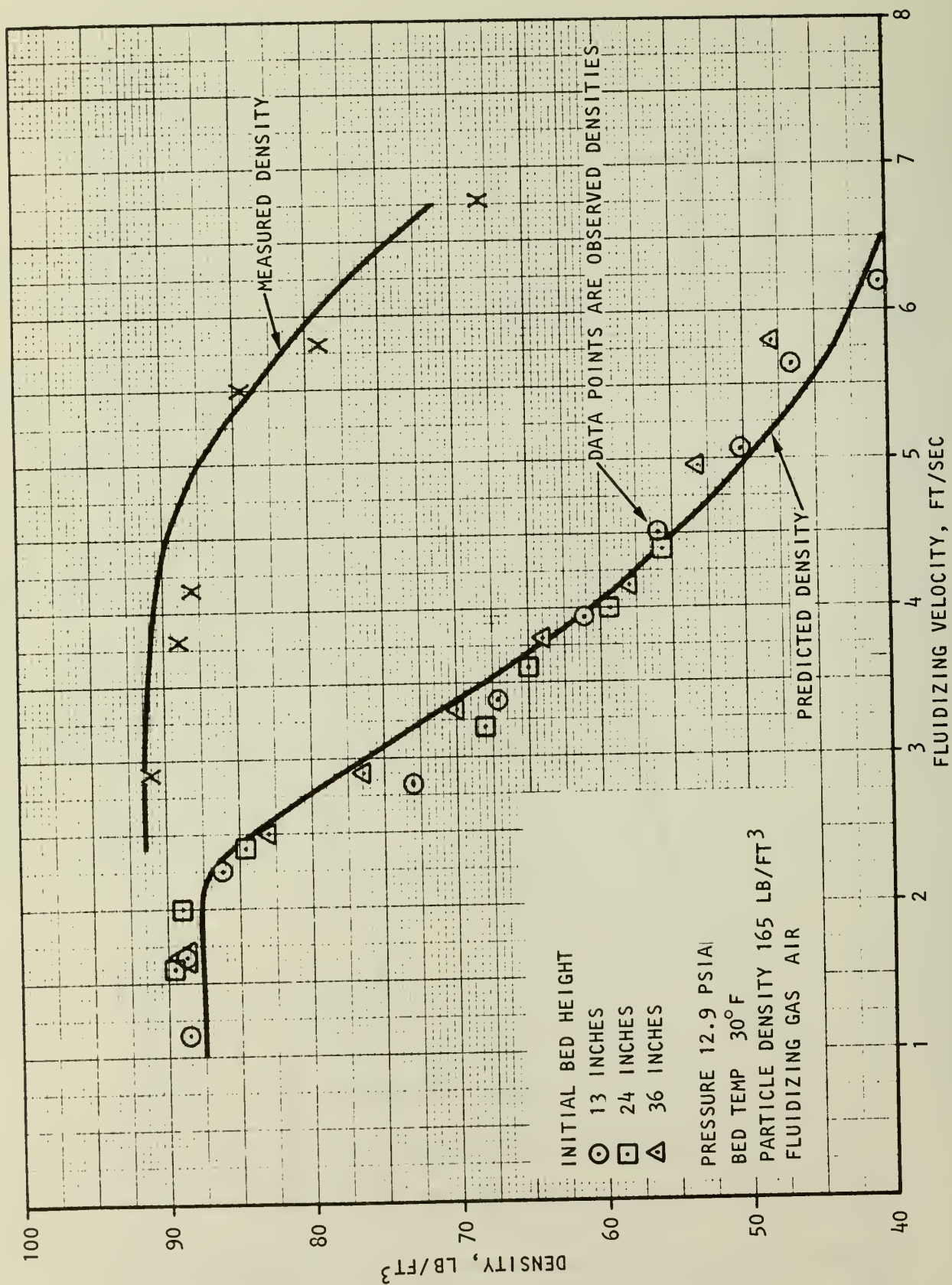
Figure 5-3. 12 INCH GLASS MODEL FLUIDIZATION TEST LIMESTONE, 6 x 16 TYLER MESH

40

BED DENSITY, LB/FT³

50 — 40 — 30 — 20 — 10 — 0

MEASURED DENSITY

DATA POINTS ARE OBSERVED DENSITIES

PREDICTED DENSITY

PRESSURE   12.9 PSIA
BED TEMP   25° F
PARTICLE DENSITY 85 LB/FT³
EFFECTIVE PARTICLE DIA .018 INCHES
FLUIDIZING GAS:

CO₂   12 MOL %
N₂   88 MOL. %

0.2   0.4   0.6   0.8   1.0   1.2   1.4

FLUIDIZING VELOCITY, FT/SEC
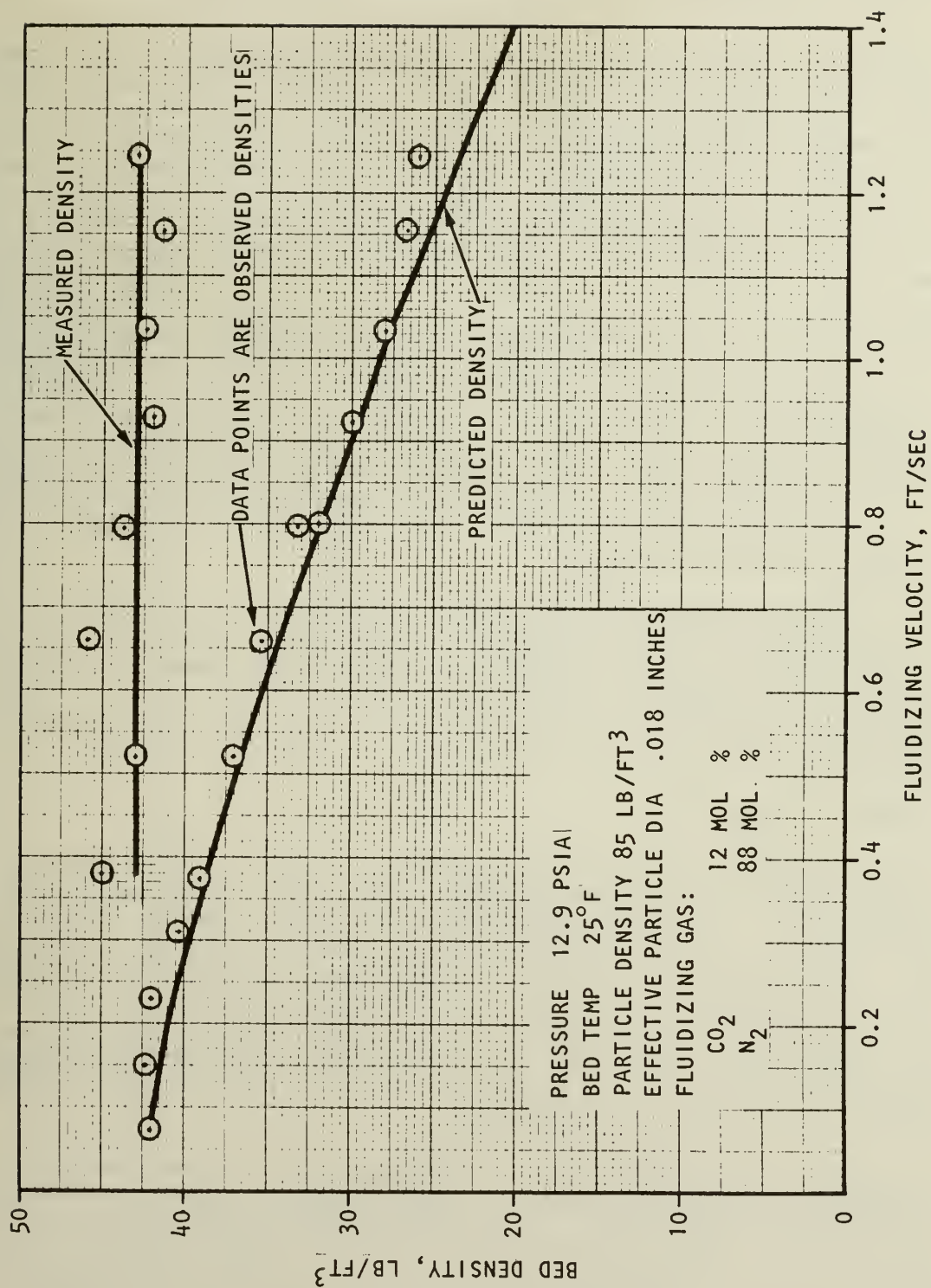
Figure 5-4.   12 INCH GLASS MODEL FLUIDIZATION TEST CHAR, 20 x 65
TYLER MESH 32 INCH INITIAL BED HEIGHT

Figures 5-3 and 5-4 show densities that have been predicted using this technique for the 12-inch diameter glass model. The excellent agreement between the observed and predicted densities lends confidence to the use of the correlation.

Subsequent to these tests, pressure differences between two side taps (one at the bottom of the straight side, the other in the vapor space above the fluidized beds in both the regenerator and the gasifier) were determined prior to several shutdowns and the drained bed material was weighed. After correcting for the relatively small amount of material in the cone or boot below the bottom tap, it was determined that the weight of the total inventory could be closely approximated by multiplying the vessel cross-sectional area by the pressure difference between the top and bottom of the bed.

The validity of the fluidized bed density correlation was also proved at full process conditions in the regenerator. Experimentally, this involved increasing the regenerator fluidizing gas velocity until the surging bed heaved large acceptor particles (6 x 10 mesh) into the external cyclone. At that point, the surging bed occupied the entire vessel (35 feet, straight side). The predicted bed density agreed within 5% of the bed density calculated from the known vessel volume and the "area x ΔP" inventory weight. Similar confirmation of the correlation in the gasifier was not practical.

Experience has shown that use of pairs of pressure taps immersed in fluidized beds allows good control of the pressure balance relationships (see Subsection 5.2.5) required in the CO_2 acceptor process. The only impact of the phenomenon illustrated in Figures 5-1 through 5-4 is that pressure tap measurements cannot be used to determine average maximum bed height of the surging fluidized beds at process conditions.

5.2.2   ACCEPTOR CIRCULATION

Acceptor material is circulated between the regenerator and gasifier through sloped standlegs and a nearly vertical lift line, as illustrated in Figure 5-5. Calcined acceptor fills the upper standleg, CD-206, to form a seal on top of a butterfly control valve, TCV-2030, which controls the solids rate to the gasifier. Recarbonated acceptor flows downward from the gasifier boot into the lower standleg, CD-204, and forms a seal over a butterfly control valve, LCV-2003, which controls the gasifier boot acceptor bed level. Recarbonated acceptor flows through the valve to the engager pot, F-222, where the solids are transported pneumatically up the lift line to the regenerator.

Standlegs were selected to aid in maintaining the system pressure balance between the two reactor vessels. Acceptor material above the butterfly control valves forms a seal. This aids in the establishment of pressure relationships which allow the solids to flow by gravity through the valves but prevents the flow of process gas through the nonfluidized acceptor.
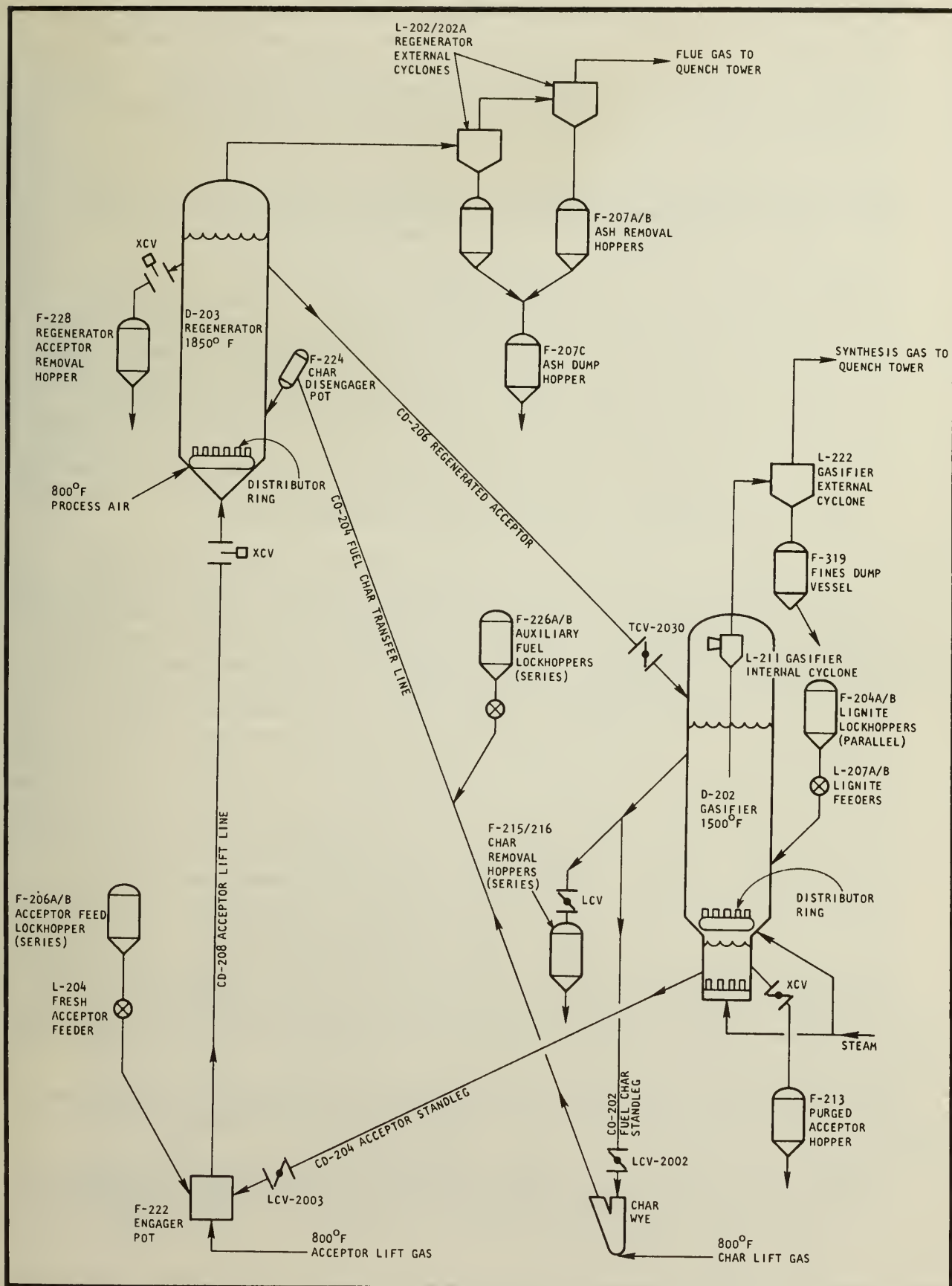
Figure 5-5.   SYNTHESIS SYSTEM (200 AREA) FLOW DIAGRAM

To help maintain constant solids flow through the standlegs, valve kickers are employed. These devices periodically increase the valve opening and then return the valve to the original control positioning. This action prevents the buildup of solids ahead of and around the valves. Gas purges are used to control the differential pressure across the valves. (Refer to Section 5.2.5.3 for a detailed discussion of the pressure balance across standlegs.)

The engager pot or pick-up chamber is designed so that the solids can flow by gravity into it and then be transferred pneumatically up the lift line to the regenerator. Air is used as the carrier gas.

Initially there was no direct measurement of the acceptor circulation rate between the gasifier and regenerator reactors. Values could be obtained only after performing time-consuming heat and material balances which required laboratory data that were not immediately available. There was a need for a rapid method of approximating circulation rate for quick adjustment of process conditions. Bench-scale studies indicated that circulation rate could be correlated with pressure drop in the lift line.[1] Therefore a testing program was conducted, initiated during pilot plant Run No. 16, and continued during all subsequent integrated pilot plant runs to provide an independent means of measuring the approximate acceptor circulation rate using existing pilot plant instrumentation.

The experimental procedure was developed to coincide with that stage in pilot plant startup when the regenerator had been filled with dead-burned dolomite (inert acceptor) but prior to the addition of char. Circulation of dead-burned dolomite was established between the reactors. In the absence of char, the dolomite showered through an empty gasifier, allowing the steady-state conditions to be quickly established in the upper section. The inert acceptor collected in the gasifier boot where sufficient gas flow was provided to incipiently fluidize the collected acceptor. By setting the position of the upper standleg flow control valve, TCV-2030, and using the lower standleg flow control valve, LCV-2003, to maintain a constant bed level in the gasifier boot, the rate of solids in and out of the gasifier was equalized. The acceptor bed level in the gasifier boot was determined by differential pressure measurements. When steady-state conditions were achieved, the lift line pressure drop and gas flow rate were recorded. Then, without changing the position of TCV-2030, the gasifier boot inventory was drained to a low level by further opening the bottom standleg flow control valve, LCV-2003. When the desired low level was attained, LCV-2003 was closed and the time required to fill the gasifier boot with solids was recorded. Typically, this procedure was performed for several circulation rates, but during selected pilot plant runs both lift gas velocity and circulation rate were varied.

Since the gasifier boot cross-sectional area was known, the circulation rate could be easily calculated using the following equation:

(1) Phase II, "Bench-Scale Research on CGS Process-Studies on Mechanics of Fluo-Solids Systems," Jan. 1970, R & D Rpt. No. 16, Interim Rpt. No. 3, Book 1, NTIS: PB-184718/AS.

$$W = \frac{\rho \Delta LA}{T} \qquad (5\text{-}2)$$

Where: W = Flow rate of solids, lb_m/hr
ρ = Bulk density of solids lb/ft^3
A = Boot cross-sectional area, ft^2
ΔL = Change in boot solids level, ft
T = Boot filling time, hrs

Alternatively, since the pressure drop across an incipiently fluidized bed of solids is equivalent to the weight of the solids per unit area, W may also be represented by:

$$W = \frac{g_c \Delta PA}{gT} \qquad (5\text{-}3)$$

Where: g_c = Newton's constant, $32.174 \dfrac{ft\text{-}lb_m}{lb_f\text{-}sec^2}$

g = Acceleration of gravity, $32.2\ ft/sec^2$

ΔP = Change in pressure drop across fluidized bed, lb_f/ft^2

Because the lift line pressure tap locations differ markedly in elevation, the density difference between the cold purge gas (80°F) and hot lift gas (1100-1500°F) was considered. This density difference generates a significant pressure head which lowers the observed value. Therefore, the measured value was corrected by calculating the head due to density difference and adding the result to the measured lift line pressure drop. The following equation was used to determine the correction factor:

$$C = \frac{g(\rho_1 - \rho_2)L}{g_c} \qquad (5\text{-}4)$$

Where: C = Differential pressure correction, lb_f/ft^2
ρ_1 = Density of purge gas, lb_m/ft^3
ρ_2 = Density of lift gas, lb_m/ft^3
L = Elevation between pressure taps, ft

In addition to the density difference, the pressure drop measurement was also corrected for any shift in the transmitter zero reading. The zero shift was determined by comparing measured pressure drops, corrected for the density difference effect, for several lift gas flows (no solids circulation), with the pressure drop predicted by the Fanning equation. Since the slopes of the predicted versus measured pressure drop curves were equal to 1, the displacement of the intercept from zero was assumed to represent pressure transmitter zero shift. The zero shift was actually used to correct for all accumulated measuring errors and was small, normally being less than 1 inch of water column.

Representative pressure drop data for the upper section of the lift line are plotted as a function of circulation rate and lift gas velocity in Figure 5-6. The pressure drop over the upper section of lift line was chosen as a correlating basis in order to avoid the influence of particle acceleration. The plots illustrate the typical U-shaped curves which were obtained.

The shape of these curves demonstrated that there was an optimum lift gas velocity. Results of the tests indicated that the optimum superficial gas velocity ranged from 50-65 ft/sec, depending upon the acceptor circulation rate. Such plots are valuable, since regions of unstable operation can be determined and avoided. Instability can occur if the lift line is operated in the region on the far left of the U-shaped curve since the line tends to load up with solids. Stability is assured for gas velocities equal to the minimum value or above. In this flow regime the solids are maintained in dilute phase flow. However, operation at velocities above the minimum is not warranted, because the higher velocities increase the erosion rate in the lift line.

It must be remembered that the circulation rate curves were developed using dead-burned dolomite as the material circulated. Because the acceptor particle properties are changed when the dead-burned dolomite inventory is replaced with active acceptor, the curves can only be used as an approximation of the true circulation rate. The actual or true circulation rate must be determined through detailed heat and material balances.

Curves such as those presented in Figure 5-6 were used to determine approximate circulation rates during a pilot plant run, since values of the lift gas velocity and upper lift line pressure drop were readily available. For control of process conditions, it was necessary to know relative changes in circulation rate but not the actual circulation rate.

5.2.3   FUEL CHAR TRANSFER

The gasifier char bed is composed of three materials: char, acceptor and intermediate fines. Since the relative proportions of these materials can and do vary considerably, an infinite number of fuel char transfer rates can be represented by the same lift line differential pressure drop. Therefor, no attempt was made to correlate the char transfer line pressure drop with fuel char rate. Knowledge of the actual fuel char rate is not needed for proper control of the regenerator operation. The operator need only know if the fuel char rate is too low or too high. This can be determined by knowing the regenerator temperature and flue gas CO concentration. The actual fuel char transfer rate can only be determined accurately by detailed heat and material balance calculations.

5.2.3.1   Flow Control

The char transfer rate from the gasifier to the regenerator is controlled by the solids controls valve, LCV-2002. (See Figure 5-7.) Two methods were used to regulate the char transfer rate. Starting in Run 4 (when char transfer was established for the first time) and up to Run 8, a
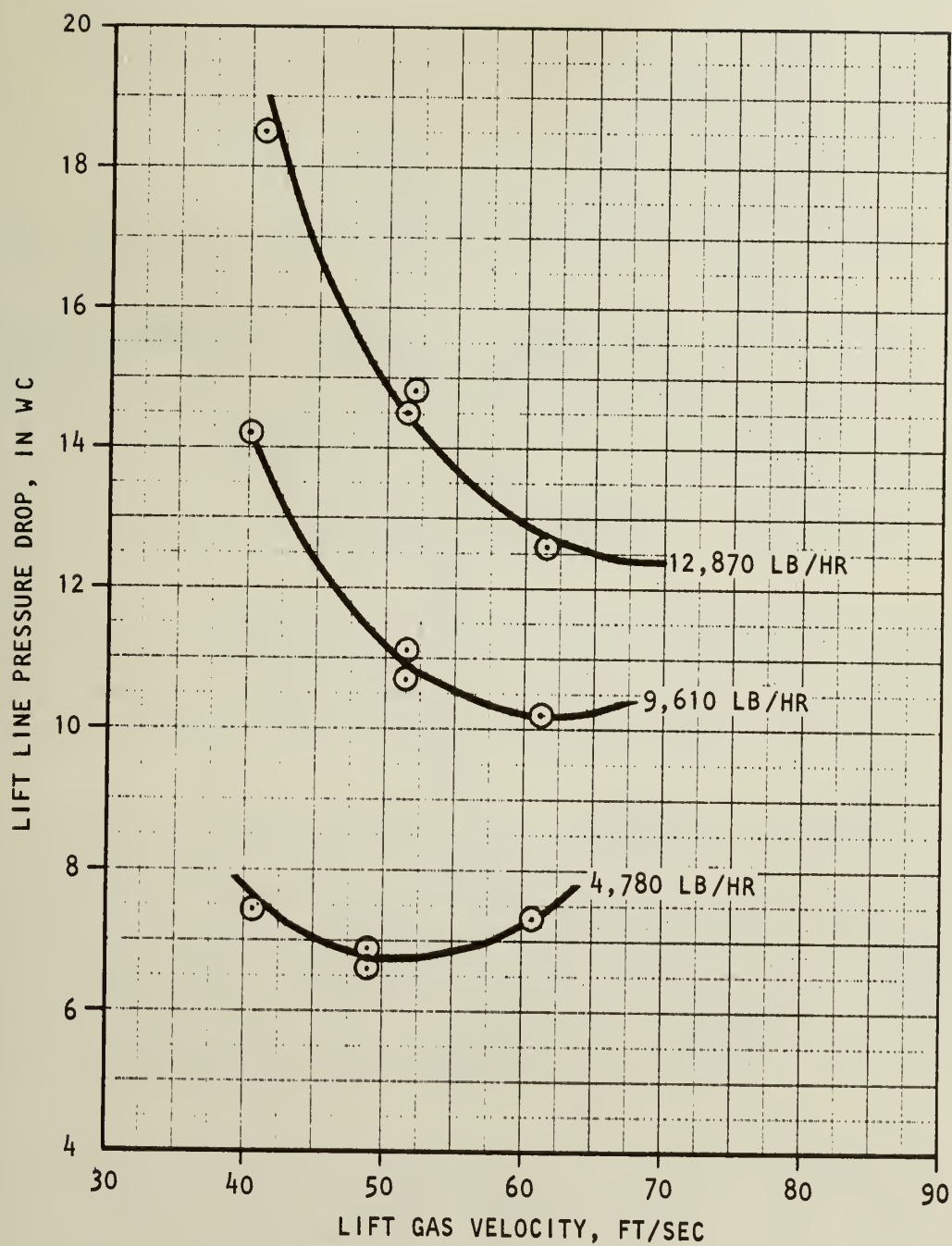
Figure 5-6. LIFT LINE PRESSURE DROP AS A FUNCTION OF LIFT GAS
RATE AND SOLIDS CIRCULATION, RUN 22C
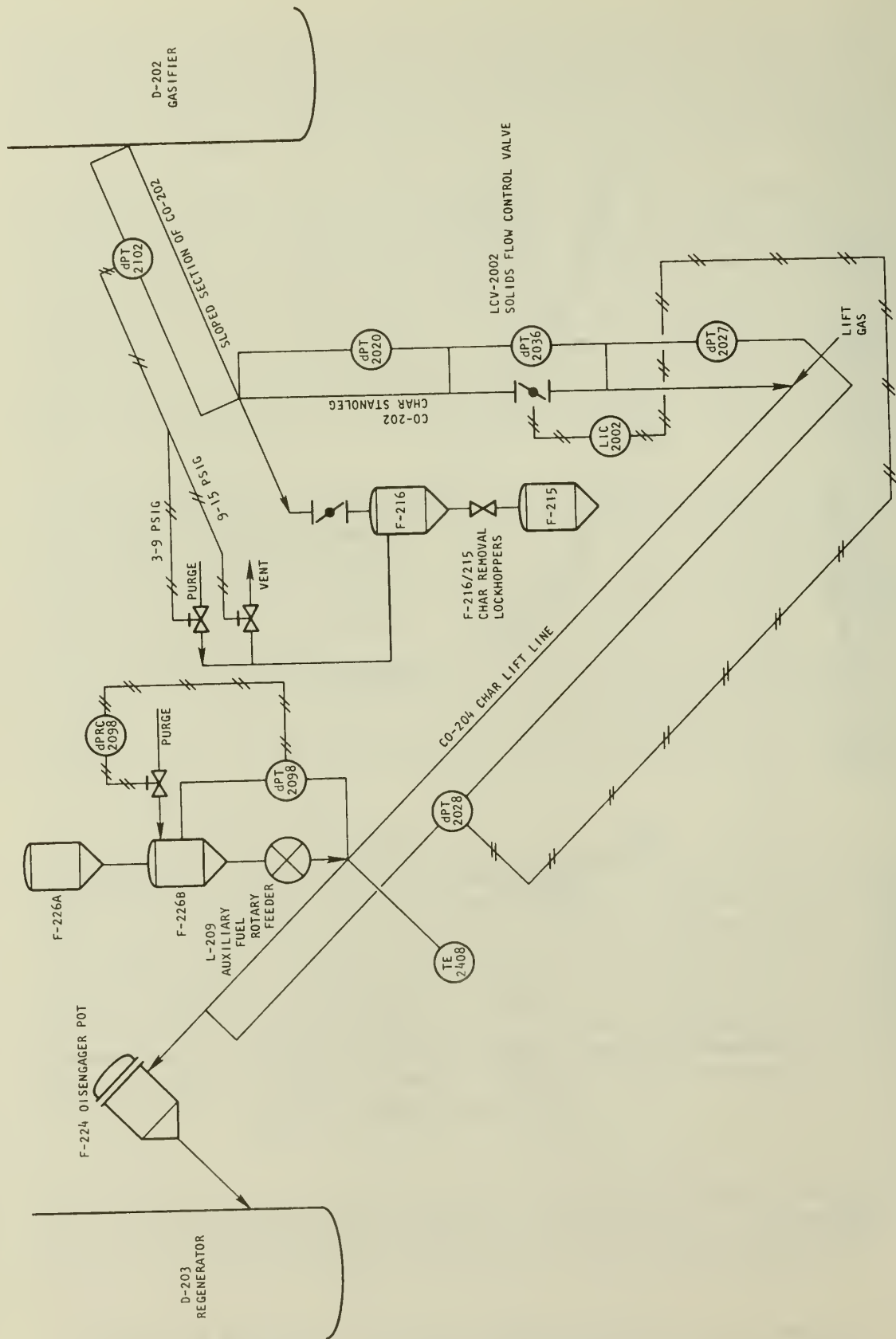
Figure 5-7. CHAR TRANSFER SYSTEM

48

constant valve positioning on LCV-2002 was maintained in order to obtain
a certain solids flow. Char transfer was erratic and unstable using this
control method, so the system was modified prior to Run 9. In the new
system, a constant differential pressure, dP-2028, across the char lift
line is sought by allowing the LCV-2002 valve positioning to be controlled
by the dPT-2028 signal. The pressure drop in the lift line is due partly
to the gas flow, which is held constant, but is increased greatly by the
presence of solids in the line. The pressure drop in the lift line de-
pends strongly upon the amount of solids in the lift line, so dPT-2028
indicates the solids flow rate in the lift line. A high differential
pressure above the set point value would cause LCV-2002 to close in
order to decrease solids flow and lower dP-2028. Similarily, a dPT-2028
value below the set point would cause LCV-2002 to open. This control
system worked very well and was used for the remainder of the runs.

The total fuel feed rate to the regenerator, which includes char from the
gasifier plus the auxiliary fuel, is used to control the CO level in the
regenerator. A high CO level is reduced by lowering the total fuel feed
to the regenerator. This is accomplished by lowering the set point on
LIC-2002 so that LCV-2002 closes down. The char transfer rate from the
gasifier will fall off and (as a result of less fuel being fed to the
regenerator) the CO level will decrease. Similarly, to raise the CO
level the set point on LIC-2002 is raised so more char is transferred
to the regenerator from the gasifier.

The use of a level controller, LIC-2002, to control differential pressure,
dPT-2028, may be confusing to the reader. Often in the pilot plant existing
instrumentation loops were modified such that the original descriptive
nomenclature no longer applied. However, the original naming was often
retained to avoid the need to change all references to the original equip-
ment.

The auxiliary fuel feed system is used to simulate the commercial practice
of utilizing recovered gasifier overhead char fines as regenerator fuel,
as well as to control the gasifier char bed level so that coal feed to
the gasifier can remain constant. When the char bed level rises, the
auxiliary fuel feeder rate is decreased manually. This decreases the amount
of solids in the char lift line, so dP-2028 will fall. As dP-2028 falls
off, LCV-2002 will automatically open and gradually drain the gasifier
char bed, lowering the bed level. Similarly, a low gasifier char bed
level is corrected by increasing the auxiliary fuel feed rate so that
dP-2028 will rise and signal LCV-2002 to close down.

Attempting to control the gasifier bed level by varying the coal feed
rate is less satisfactory. Changes made in the relatively cool, fresh
feed rate have more of an effect on the gasifier char bed temperature than
changing the char withdrawal rate. Additionally, because of the volatile
yield from the lignite feedstock, changes in the feed rate result in sub-
stantial changes in the gasifier product gas rate. It is preferable to
maintain a constant feed rate to the gasifier.

5.2.3.2 Operation

Some problems were initially experienced with char transfer. The main cause of char transfer upsets stemmed from sudden changes in the purge gas flow in the CO-202 standleg. Due to the system pressure balance, purge gas flows against the downward flow of solids in the line. A change in the system pressure balance can cause a change in the purge gas flow rate or direction. Sudden changes in the purge gas flow often caused char fines to accumulate and form plugs in the standleg. This led to loss of char transfer.

Fines plugs formed more often in the sloped section of the standleg than in the vertical section. Char transfer was more sensitive to purge gas flow changes in this sloped section than in the vertical section. Solids in the sloped section will fluidize at a lower gas velocity than solids in the vertical standleg, allowing fines to hold up in the standleg. Further discussion of this phenomenon and its operational consequences is considered in Subsection 5.2.5 of this report. Solids flow may also have been hindered by the bend in the standleg at the end of the sloped section. The bend provides a place for fines to accumulate and form plugs.

The problems associated with standleg gas flow changes were largely corrected by making piping changes in the char transfer system. For Run 11, the 2-inch diameter char standleg, which included both the sloped and vertical sections of the char standleg, was replaced with a 3-inch diameter line. Prior to Run 33, the sloped line section of the char standleg was again modified. The 3-inch diameter pipe was replaced with a 4-inch diameter line. These line size increases have the effect of decreasing the purge gas velocity in the sloped section of the standleg. The lower gas velocity minimizes stripping of char fines from the bulk solids flow and, therefore, prevents solids plugs from forming. These modifications made during the course of the pilot plant program greatly improved the reliability of the char transfer system.

Another source of char transfer instability was the char removal system. The char removal system was used for several runs as a means of controlling the buildup of intermediate fines in the gasifier char bed. The original char removal system included two lockhoppers arranged in parallel. Whenever operation was switched between the lockhoppers, pressure inbalance between the lockhoppers and the sloped section of the char transfer standleg frequently caused a sudden change in gas flow in the sloped section of the char standleg, resulting in the plugging of the line.

In order to improve the stability of the char transfer system, the parallel char removal system was changed to a series system in Run 26. (See Figure 5-7.) In the series system the lockhopper receiving char directly from the standleg is continuously onstream, so that switching between lockhoppers is avoided. In addition, an automatic purge and vent system was set up for the lockhoppers so that the pressure drop, dP-2102, across the sloped standleg would remain constant. Gas would be purged into the lockhoppers when the dP-2102 pressure drop was low. The lockhoppers would be vented if the pressure drop was too high.

The series system proved to be an improvement over the parallel system. Char transfer was more stable and upsets occurred less frequently.

In the commercial plant design, piping changes were made to the char transfer system that should completely eliminate transfer problems. The standleg was lengthened in order to increase the seal formed by the head of solids in the standleg. With the larger head of solids, the purge gas flow rate (SCFH per sq. ft. of line cross section) can be proportionally lower for a given pressure drop across the total length of the standleg, as compared to the present pilot plant standleg. Also, the sloped section of the standleg represented a smaller portion of the total standleg length and the angle of the bend was widened. This has the effect of increasing the vertical component of the standleg and minimizing the troublesome bend in the line.

The char removal system was installed in the pilot plant as an expedient solution to the problem of the buildup of intermediate fines in the gasifier char bed. The char removal system was taken out of service prior to Run 33 when a better method (F-228 spent acceptor removal system) was devised for controlling intermediate fines accumulation in the gasifier. An acceptor withdrawal system similar to that of the F-228 system was designed for the commercial plant so the char removal system would not be incorporated into a commercial plant.

When char transfer is lost the usual procedure to recover transfer is to close off the standleg, purge the standleg clear of solids, allow the standleg to refill with solids, and then open up the flow control valve, LCV-2002. An in-house designed rotating wafer valve that was installed just above LCV-2002 prior to Run 39 is used to seal off the standleg while the line is being refilled. When char transfer is being re-established, the differential pressure between the gasifier and regenerator is sometimes increased temporarily to reduce the pressure drop across the standleg. The differential pressure between the gasifier and regenerator must be lowered back to its original position once char transfer is established, in order to prevent a system pressure imbalance. The pressure imbalance could cause steam to backflow from the boot into the recarbonated acceptor standleg, CD-204.

5.2.4 INTERFACE CONTROL

In the gasifier boot, because the gas velocity is sufficiently low, acceptor showers out of the char bed to form a fluid bed of acceptor. The char particles, however, are lighter and smaller in size than the acceptor, and are therefore stripped away from the acceptor and forced back up into the char bed. Acceptor is withdrawn from the bottom of the boot into the recarbonated acceptor standleg, CD-204, to maintain a constant acceptor inventory.

A sharply defined interface exists in the upper part of the boot between the char and the acceptor bed. The interface is the point of greatest char penetration into the boot before the char is stripped from the acceptor by the fluidizing gas.

Separation of acceptor from the char bed is necessary in order to independently control the rates of char and acceptor transfer from the gasifer to the regenerator. A mixture of char and acceptor is withdrawn from the gasifier char bed and transferred to the regenerator through the char standleg and lift line. However, while this stream may satisfy the regenerator fuel char requirements, not enough acceptor is contained in the mixture to satisfy the required acceptor circulation rate in the system. More acceptor needs to be withdrawn from the gasifier and sent to the regenerator for calcination. The separated acceptor from the bottom of the boot can be fed to the regenerator independent of char transfer. In order to maintain the necessary acceptor circulation rate in the system, acceptor flow rates across the interface are necessarily high. Acceptor mass fluxes across the interface in the pilot plant are typically between 6000-12,000 lb/(hr)(ft^2).

Both an overly expanded bed and a nonfluidized acceptor bed in the boot are to be avoided. With an overly expanded bed, the boot fluidizing velocity is high enough to hinder the showering of acceptor down into the boot. In addition, backmixing of acceptor and char is appreciable. Backmixing disturbs the interface because acceptor is held up and prevented from showering down through the char bed. A nonfluidized bed is undesirable because it does not allow the location of the interface to be determined by the differential pressure instruments. In addition, if the boot is not fluidized, char is entrained below the interface by the downward moving acceptor.

Control of the interface level so that it remains well within the boot is critical. The interface level is located and controlled by three differential pressure instruments. (See Figure 5-8.) The pressure taps for dPT-2083 are across the lower part of the boot that normally contains only acceptor. The interface is usually between the pressure taps for dPT-2002; dPT-2001 reads the differential pressure across the transition section which, under normal operating conditions, contains the char-acceptor bed.

Two other differential pressures were also recorded, as shown in Figure 5-8. These were dP's 2111 and 2112. The transmitter signal lines for these dP's were connected to the pressure taps used by the other three boot differential pressure transmitters. Both dPT-2111 and 2112 were set up to read the differential pressure across large portions of the bed and overlapped each other. Infrequently, they were used for short periods to locate the interface level whenever a plugged pressure tap would put one of the other differential pressure transmitters out of service. These additional taps allowed the interface to be controlled while the plugged tap was cleared.

The dPT-2002 signal was used to regulate the interface level. The differential pressure signal controlled the positioning on LCV-2003, opening the valve if the interface rose above the instrument control set point, and closing down on the valve if the interface level dropped. This control system worked well and was able to maintain a steady interface level.
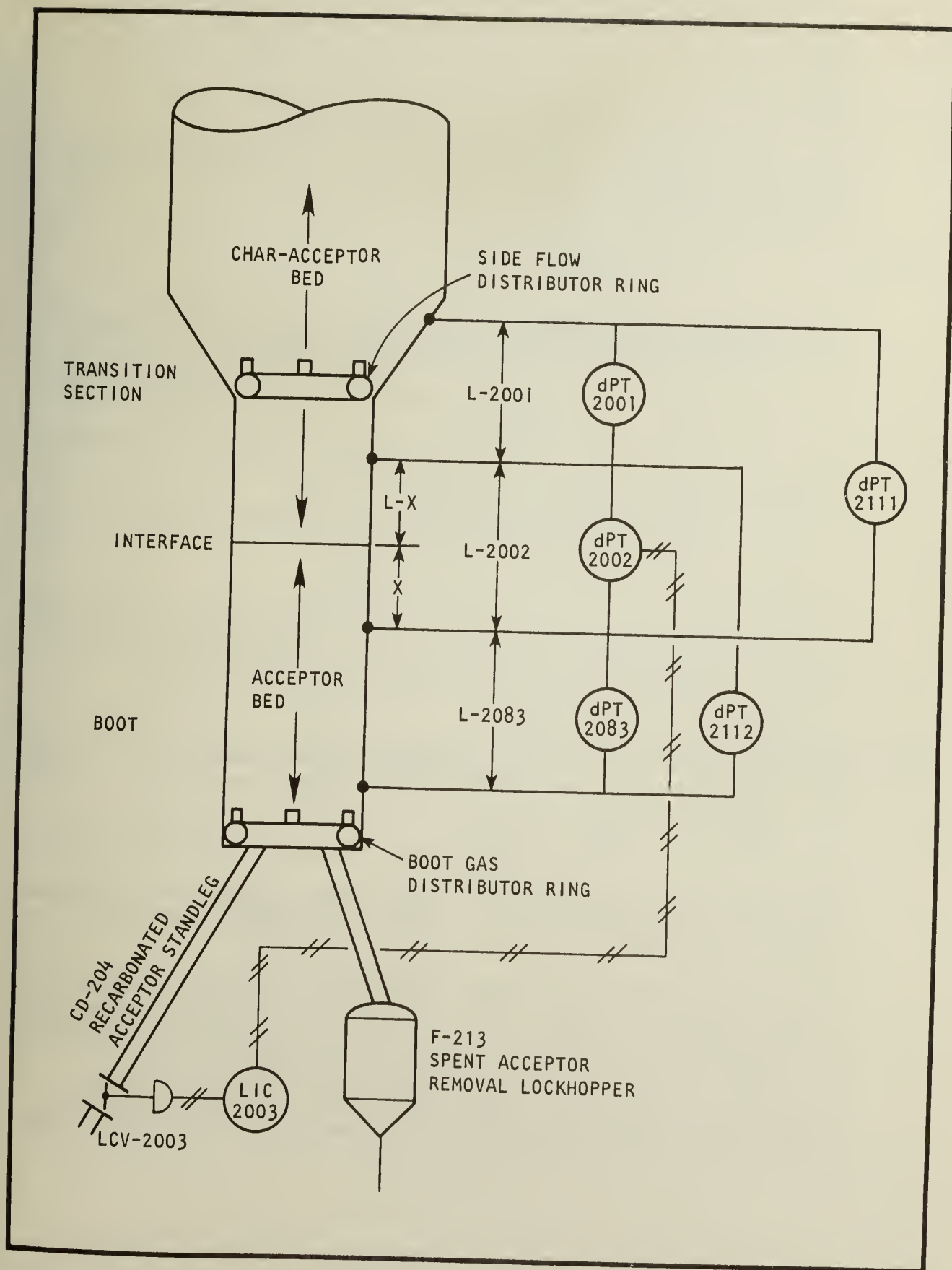
Figure 5-8.   CHAR - ACCEPTOR INTERFACE CONTROL INSTRUMENTATION

It was desired to set the transmitter ranges on dPT-2083, 2002, and 2001 so that bed density would be equal to the chart recorder readings. However, the acceptor bed density exceeded 100 lb/ft^3 whenever dead-burned dolomite was in the system. Therefore, it was necessary to increase the transmitter range so the recorder pen would be on chart for all materials used. The ranges were set up so bed density could be determined from chart readings multiplied by a single factor.

To determine the required transmitter ranges, consider the following equation relating bed density to the pressure drop of the gas flowing through the bed of fluidized solids:

$$\Delta P = \frac{\rho \text{ Bed } L}{62.4} \ (g/g_c) \tag{5-5}$$

Also the differential pressure is determined from the recorder chart reading and transmitter range (inches water column) by:

$$\Delta P = \frac{\text{Chart reading}}{100\%} \times \text{Range} \tag{5-6}$$

ΔP = Pressure drop, inches water column
ρ Bed = Apparent density of fluid bed, lb/ft^3
L = Distance between transmitter pressure taps, inches
g = Acceleration due to gravity, ft/sec^2
g_c = Newton's constant, $32.174 \ \dfrac{\text{ft} \cdot \text{lb}_m}{\text{lb}_f \text{Sec}^2}$

It was desired that the chart reading times a simple factor be equal to the bed density (in this case, the factor is 1.5) so that:

$$\rho \text{ Bed} = 1.5 \times \text{Chart reading} \tag{5-7}$$

Substituting Equation 5-7 into 5-5 and combining Equations 5-5 and 5-6, the following result is obtained for the instrument range:

$$\text{Range} = 1.5 \times \frac{100}{62.4} \ (g/g_c) \ L \tag{5-8}$$

The range is determined only by L, the distance between the two pressure taps, which has already been set up by the physical arrangement of the taps in the vessel.

Since the char-acceptor interface level cannot be visually observed, its location must be calculated from the differential pressure readings of dPT's-2083, 2002, and 2001. The interface is located somewhere between the pressure taps of dPT-2002. The pressure taps of dPT-2083 are submerged only in the acceptor bed, so the instrument reading can be used to calculate the acceptor bed density. Similarily dPT-2001 pressure taps are submerged only in the char bed, so the char bed density can be determined from this reading.

Referring to Figure 5-8, the differential pressure read by dPT-2002 is composed of the pressure drops due to the acceptor bed portion (of height 'X' up to the interface) and the pressure drop due to the char bed portion above the interface (to height L-X):

$$\Delta P_{L2002} = \Delta P_X + \Delta P_{(L-X)} \qquad (5-9)$$

Substituting Equation 5-6 in the left-hand side of Equation 5-9 and Equation 5-5 for the two terms on the right-hand side yields Equation 5-10:

$$\left[\frac{(\text{Chart reading})_{2002}}{100\%}\right]\left[(\text{Range})_{2002}\right] = \left[(\rho\text{dPT-2083})(X) + (\rho\text{dPT-2001})(L-X)\right]\frac{g/g_c}{62.4}$$

Where ρdPT-2083 and ρdPT-2001 are the densities for the acceptor and char beds, respectively, determined by the differential pressure measurements. Substituting the following equations, derived by combining Equations 5-5 and 5-6

$$\rho\text{dPT-2083} = \frac{(\text{chart reading})_{2083}}{100\%}\;(\text{Range})_{2083}\;\frac{62.4}{L_{2083}}\;\;g_c/g \qquad (5-11)$$

$$\rho\text{dPT-2001} = \frac{(\text{Chart reading})_{2001}}{100\%}\;(\text{Range})_{2001}\;\frac{62.4}{L_{2001}}\;\;g_c/g \qquad (5-12)$$

into Equation 5-10 yields, for the fraction of L_{2002} that the interface has risen; Equation (5-13):

$$\frac{X}{L_{2002}} = \frac{\left[\dfrac{(\text{Chart reading})_{2001}\;(\text{Range})_{2001}}{L_{2001}}\right] - \left[\dfrac{(\text{Chart reading})_{2002}\;(\text{Range})_{2002}}{L_{2002}}\right]}{\left[\dfrac{(\text{Chart reading})_{2001}\;(\text{Range})_{2001}}{L_{2001}}\right] - \left[\dfrac{(\text{Chart reading})_{2083}\;(\text{Range})_{2083}}{L_{2083}}\right]}$$

Substituting equations similar to Equation 5-8:

$$(\text{Range})_{2002} = 1.5\;\frac{(100)}{62.4}\;(g/g_c)\;L_{2002}$$

$$(\text{Range})_{2001} = 1.5\;\frac{(100)}{62.4}\;(g/g_c)\;L_{2001}$$

$$(\text{Range})_{2083} = 1.5\;\frac{(100)}{62.4}\;(g/g_c)\;L_{2083}$$

for the respective ranges in Equation 5-13 yields:

$$\frac{X}{L_{2002}} = \frac{(\text{Chart reading})_{2002} - (\text{Chart reading})_{2001}}{(\text{Chart reading})_{2083} - (\text{Chart reading})_{2001}} \qquad (5\text{-}14)$$

Equation 5-14 reveals that the relative location of the interface can be ascertained from just the three differential pressure recorder chart readings when the instruments are ranged according to Equation 5-8.

The interface can also be located graphically by a plot of the bed pressure drop at different heights in the gasifier and boot. An example, with data taken from Run 47B, is shown in Figure 5-9. The pressure drop ordinate values are the pressure differences between the high side pressures of the various differential pressure trans- mitters and the gasifier exit pressure (150 psig). The abscissa is the height above the boot flange at which the high side pressure taps are located. The pressure drop per foot of bed remains constant for the char bed, but a discontinuity occurs at the interface level. Here the pressure drops per foot of bed increases sharply because of the gas flow through the more dense acceptor bed in the boot. The interface level is located at the intersection of the extrapolated lines for the char bed and the acceptor bed. Plots like these were made for some of the early runs in order to determine if the interface was actually estab- lished during the run.

Since the separation of char and acceptor is essential to the process, the stability of the interface is critical. Factors affecting inter- face stability include:

(1) Density difference between the char and acceptor.
(2) Boot gas flow.
(3) Ability to transfer acceptor through the lower acceptor standleg, CD-204.

A large density difference between the char and acceptor is highly desirable. It increases the preferential settling of the more dense acceptor out of the char bed while the lighter char is stripped away. If the difference in densities is small, it is extremely difficult to separate the char and acceptor and maintain the interface.

In the pilot plant, bed densities for the acceptor bed were typically about 60-65 lb/ft^3 and about 30-35 lb/ft^3 for the char bed. The difference in these densities proved to be sufficient to maintain a stable interface.

Generally, the char-acceptor interface was stable. However, unstable interfaces often resulted when subbituminous coal was used for feedstock and limestone was used as acceptor. The acceptor material acquired a low particle density that prevented a stable interface from being main- tained. Additional details covering the interface control problems associated with the use of subbituminous coal feedstock are given in Run Report 44, Volume 8.
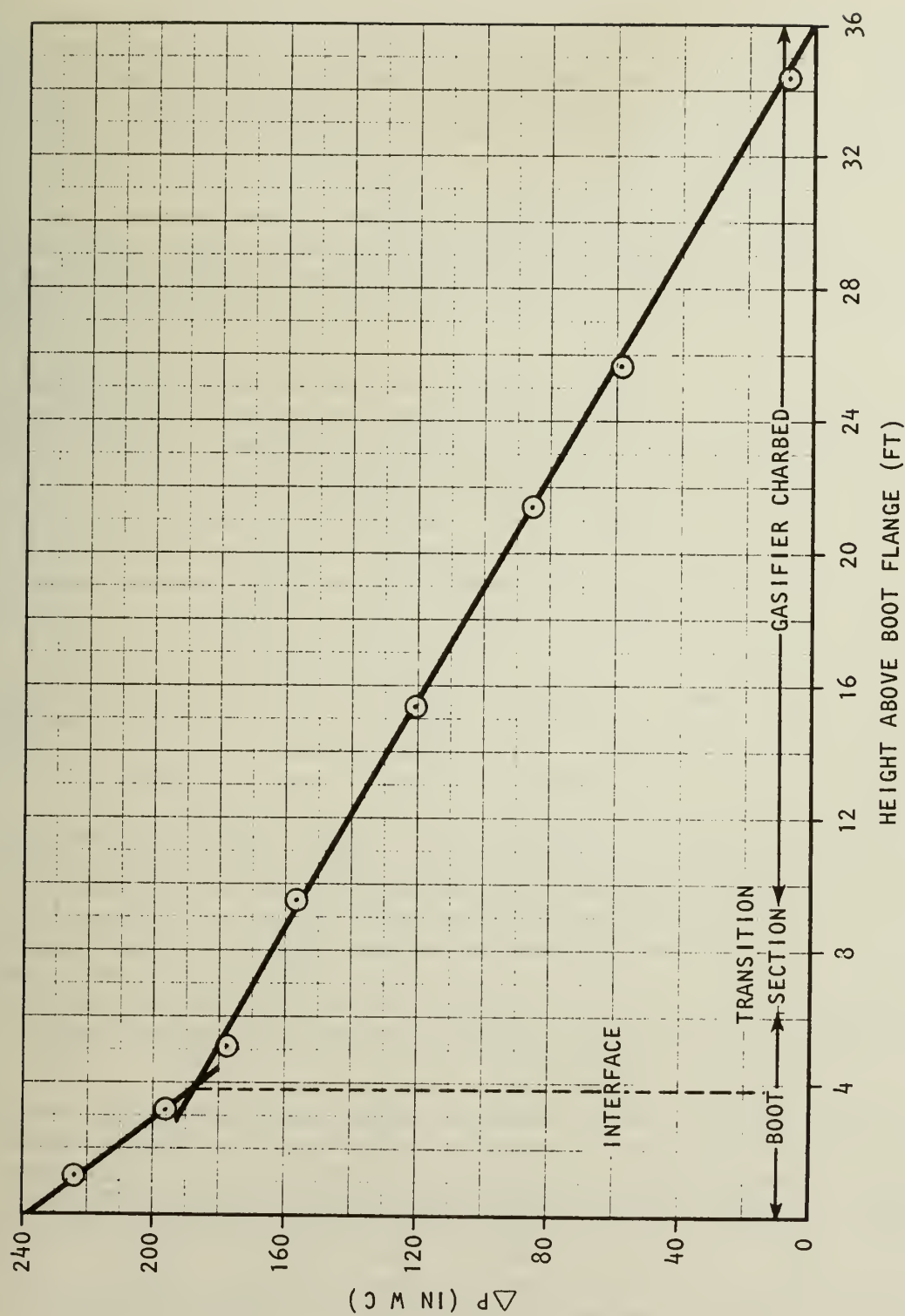
Figure 5-9. INTERFACE LOCATION FROM CHAR BED AND ACCEPTOR BED
PRESSURE DROP CHANGES

57

Gas flow is also critical in order to maintain a stable interface. The gas flow should be such that the boot gas velocity is slightly greater than the incipient fluidization velocity for the acceptor. The superficial boot velocity in the pilot plant was generally about 2 fps.

It is important that the boot gas velocity be sufficient to prevent char from falling down into the lower part of the boot. If the acceptor is at incipient fluidization, then the char will be stripped away from the acceptor. The 2 fps boot velocity in the pilot plant was sufficient for char stripping.

Sudden changes in boot gas flow were the source of most problems with interface stability. Either a decrease or increase in flow could upset the interface. Severe boot upsets occurred on several occasions, due to the malfunctioning of the boot steam flow control valve and flow control instrumentation.

Another source of boot upsets was the operation of the spent acceptor dump hopper, F-213. When the F-213 hopper was in operation, bringing it onstream after a dumping cycle was hazardous if the lockhopper pressure was not equalized with that of the boot. Gas would vent into the boot from the lockhopper if the lockhopper was overpressurized, or boot gas would flow into the lockhopper if the lockhopper was underpressurized. Either situation could cause a boot upset because the boot gas flow rate would be suddenly changed. This problem was solved by discontinuing the removal of spent acceptor through the F-213 lockhopper and moving the withdrawal site to a nozzle on the regenerator reactor.

Loss of acceptor transfer through the CD-204 was an infrequent occurrence. Pieces of a boot deposit on occasion fell into the standleg and blocked any further flow of acceptor. A few times, pieces of spalled refractory became lodged in the standleg and prevented acceptor transfer.

When acceptor transfer through the standleg was blocked, the interface level would start to rise as acceptor continued to shower down into the boot. It is crucial that the interface never be allowed to rise into the transition section, because the gas velocity in the transition section is not sufficient to fluidize collected acceptor. The formation of solids bridges or "caps" has often occurred when acceptor was allowed to defluidize in the transition section. At times, sufficient gas flow to the gasifier could not be provided to break up the bridges (plugs). Therefore some runs were terminated.

A successful procedure was developed to regain lost interfaces or to halt a rising interface. First, acceptor circulation, acceptor make-up, and coal feed to the gasifier are stopped. Boot gas flow is then increased drastically, using recycle gas and steam, so that the boot will become completely turbulent. When conditions warrant, the interface can be re-gained by slowly lowering boot gas flow and allowing the acceptor to settle out of the char bed. As the operating personnel gained experience with handling boot upsets, recovery from the upsets was achieved often and the upsets became less of a threat to plant operation.

5.2.5   PRESSURE BALANCE

5.2.5.1   Relationships

The pressure balance of the system is determined primarily by the differential pressure between the gasifier and the regenerator. The gasifier exit pressure is controlled at 150 psig. The pressure at the regenerator exit is controlled so that it is normally about 3-6 psi lower than the gasifier exit pressure. The lower regenerator pressure causes the acceptor and char lift gases to flow preferentially to the regenerator in the lift lines, rather than to the gasifier through the char, CO-202, and lower acceptor, CD-204, standlegs. The pressure balance is critical because excessive gas flow up the standlegs could impede the downward flow of solids.

An excessively high differential pressure between the vessels is avoided to:

(1)   Prevent steam from the gasifier boot from entering the CD-204 acceptor standleg. Steam is undesirable in the CD-204 standleg, because if the temperature in the line is allowed to drop below about $1200^{o}F$ acceptor agglomeration can occur due to the formation of $Ca(OH)_2$.

(2)   Prevent process gas from the gasifier from entering the CO-202 char standleg and the CD-206 acceptor standleg.

The solids-filled standlegs acted as gas seals between the two vessels. The solids provided a resistance to gas flow into the standlegs; the longer the standleg, the greater the gas sealing effectiveness of the leg.

Purges are placed on all three standlegs to prevent process gas from entering the standleg from the higher pressure end of the line. The flow rate of purge required depends upon the length of the standleg and the overall pressure drop across the entire standleg, which is set by the differential pressure between the gasifier and the regenerator. Less purge is required to produce a given pressure drop across the standleg as the length of the standleg is increased.

Since the standleg lengths cannot be changed in the pilot plant, the purge gas rate must be varied to maintain the desired pressure drop. Yet, it is desired to minimize the purge rates so that little of the inert purge gas which is used in the CD-204 and CD-206 standlegs enters the gasifier where it would dilute the gasifier overhead gas and reduce the overhead gas heating value. In addition, high purge rates may produce gas velocities high enough to fluidize the smaller particles in a standleg. The small particles can hold up in the standlegs and form plugs that obstruct the further flow of any solids.

This is particularly a problem in the char standleg, where the lightest, finest char particles are easily stripped out of the bulk solids flow. The sloped section of the char standleg is extremely sensitive to changes in gas flow. Experimental work at the Conoco Coal Development Company Library Research Center has shown that the maximum pressure drop per linear foot of line allowed in a 60 degree sloped standleg

59

before fluidization of the particles takes place is only 40-45% of the
maximum pressure drop per linear foot of line for a vertical standleg.
In a sloped standleg, the gas bypasses much of the solids as the solids
settle to the bottom of the pipe and the gas flows in the open area
above the solids. Since the cross sectional area available for gas
flow is reduced, the gas velocity increases promoting the fluidization
and stripping of fine material at the upper periphery of the line. As
a result, a certain purge rate to the char standleg may allow stable
operation of the vertical section but cause problems in the sloped section.

A diagram of the gasifier-regenerator system and the pressure balance
arrangement is illustrated in Figure 5-10. Typical pressures at various
points, in inches of water column (W.C.) relative to Location 1 (gasifier
unit) are shown. The pressure drop across the gasifier fluid char bed
is about 150 in. W.C. and a pressure drop of about 75 inches W.C. occurs
across the fluidized boot and transition section. The pressure at Location
5, just above LCV-2003 on the CD-204 recarbonated acceptor standleg, is
typically 50 in. W.C. or more higher than the boot. This pressure relationship
is critical and is closely monitored to insure that the standleg is at a
higher pressure than the boot. Otherwise, steam may enter the standleg
from the boot. Acceptor lift gas flows up the lift line from the
engager pot and does not enter CD-204, because of the approximately
10 in. W.C. drop across the LCV-2003 valve. The pressure drop across the
acceptor lift line is typically 75 in. W.C. The pressure drop across the
regenerator bed is about 330 in. W.C., or about 12 psi. The differential
pressure between the regenerator and gasifier is about 5 psi (as measured
by dP-2030) in this example. To prevent the flow of gas from the gasifier
into the regenerator through the CD-206 acceptor standleg, the standleg is
purged with nitrogen just above the TCV-2030 valve. The purge raises
the pressure at this point as it is typically 2-5 in. W.C. higher than
the gasifier. Purge gas, therefore, flows back into the gasifier and
prevents the gasifier process gas from entering the standleg. The pressure
drop across the char lift line is about 50 in. W.C. Again, as in the CD-204
acceptor standleg, a purge is placed just above the LCV-2002 valve to pre-
vent lift gas from entering the standleg. The pressure drop across the
valve is about 10 in. W.C. The pressure drop across the entire vertical section
of the char standleg is about 135 in. W.C., while the pressure drop across the
shorter sloped section is about 15 in. W.C.

The pressure drop across the char standleg has caused problems due to the
stripping of char fines from the standleg. It is desired to minimize the
purge rate, and, hence the standleg pressure drop. An analysis of the
system pressure balance was initiated to determine what effect minimizing
the char standleg dP had on the other standleg pressure balances. Par-
ticularly, a relationship was developed between the pressure differentials
for the char standleg and the lower acceptor standleg, CD-204.

Referring to Figure 5-10, a pressure balance around the loop composed of
the lower acceptor standleg and lift line and the upper acceptor standleg
yields:

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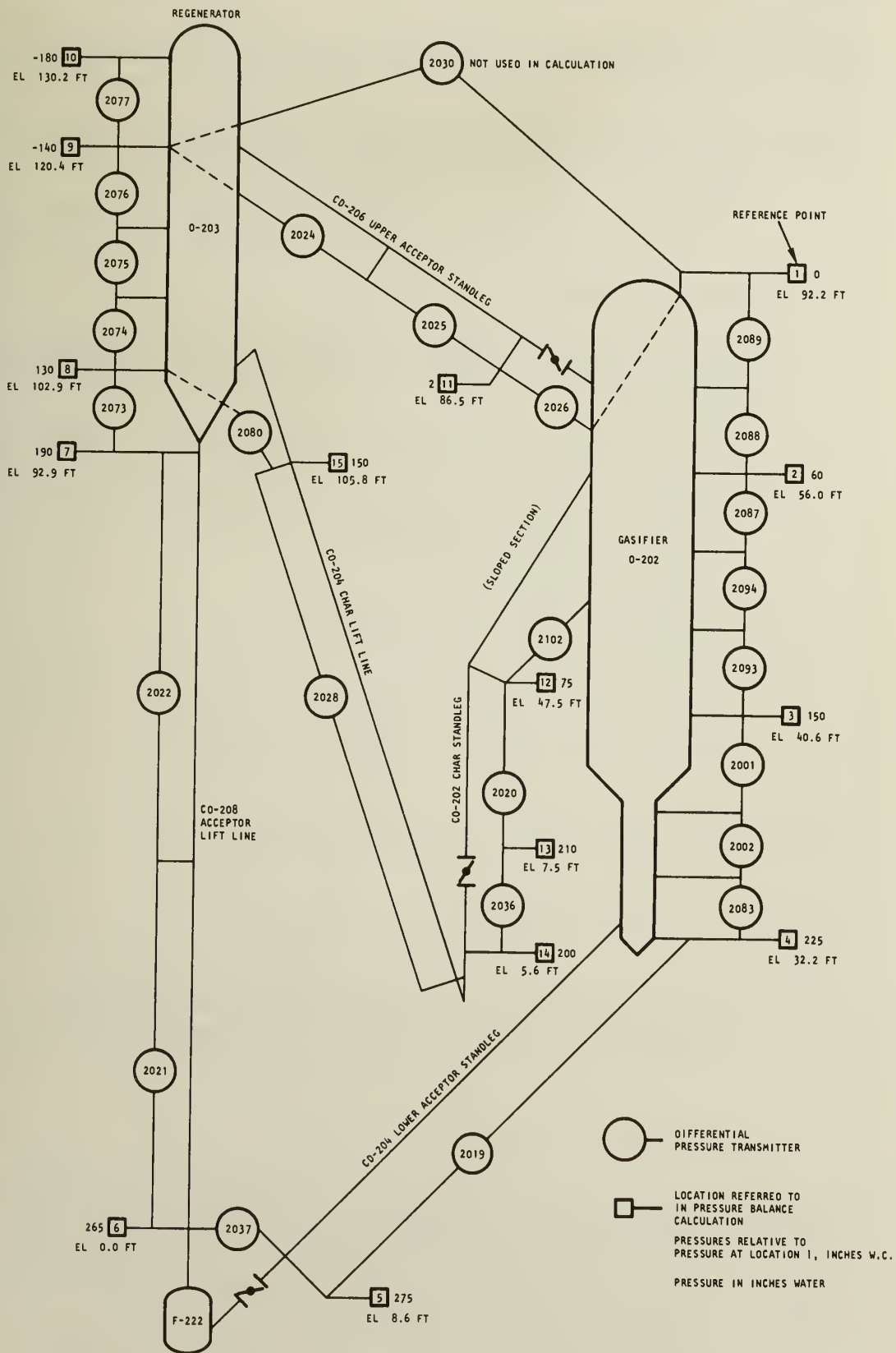
Figure 5-10. DIFFERENTIAL PRESSURE TRANSMITTER LOCATION PRESSURE
BALANCE CALCULATION

61

dP(1-2) + dP(2-3) + dP(3-4) + dP(4-5) + dP(5-6) =   (5-15)
dP(1-9) + dP(9-8) + dP(8-7) + dP(7-6)

where dP(I-J) denotes the differential pressure drop between Points I
and J.

Similarly, for a pressure balance around the char lift line and standleg
and the upper acceptor standleg, we have Equation (5-16):

$$dP(1-2) + dP(2-12) + dP(12-13) + dP(13-14) = dP(1-9) + dP(9-8)$$
$$+ dP(8-15) + dP(15-14)$$

The following is assumed:

(1)   The boot acceptor bed height is 5 feet.
(2)   The dP across the fluid beds is equal to the bed density times
     the bed height.

Let: X = dP(4-5) + dP(5-6) = dP-2019 + dP-2037, in. W.C. = dP across
      lower acceptor standleg.
      Y = dP(2-12) + dP(12-13) + dP(13-14) = dP-2020 + dP-2102 + dP-2036, in.
        W.C. = dP across char standleg.
      R_1 = Char bed density, lb/cu ft
      R_2 = Boot density, lb/cu ft
      R_3 = Regenerator bed density, lb/cu ft
      H = Char bed height above the boot, ft
      D = dP(1-9) = dP-2030, in. W.C.
      A = dP(8-7) + dP(7-6) = dP-2021 + dP-2022 + dP-2073, in W.C. =
        dP across the acceptor lift line.
      C = dP(8-15) + dP(15-14) = dP-2080 + dP-2028 in. W.C. =
        dP across the char lift line.

Employing the two assumptions, the following dP's can be defined as
(using 0.1922 to convert lbs/sq ft to in. W.C.):

$$dP(1-2) = (0.1922)(H-19.6)R_1 \qquad\qquad (5-17)$$
$$dP(9-8) = (0.1922)(17.5)R_3 \qquad\qquad (5-18)$$
$$dP(1-2) + dP(2-3) + dP(3-4) = (0.1922)HR_1 + (0.1922)(5)R_2 \quad (5-19)$$

Substituting Equations 5-17 to 5-19 and the above definitions into
Equations 5-15 and 5-16, and then combining the two equations, the
final relationship that results between the char and lower acceptor standlegs
is:

$$X = Y - 3.773 R_1 - 0.962 R_2 + A-C \qquad\qquad (5-20)$$

Equation 5-20 is presented graphically in Figure 5-11, using typical
operating values for the parameters R_1, R_2, A, and C. The figure
shows Y (the dP across the char standleg) in terms of Y/R_1L (where L
is the length of the char standleg in feet). This pressure drop factor
represents the fraction of the maximum attainable pressure drop in the
line.
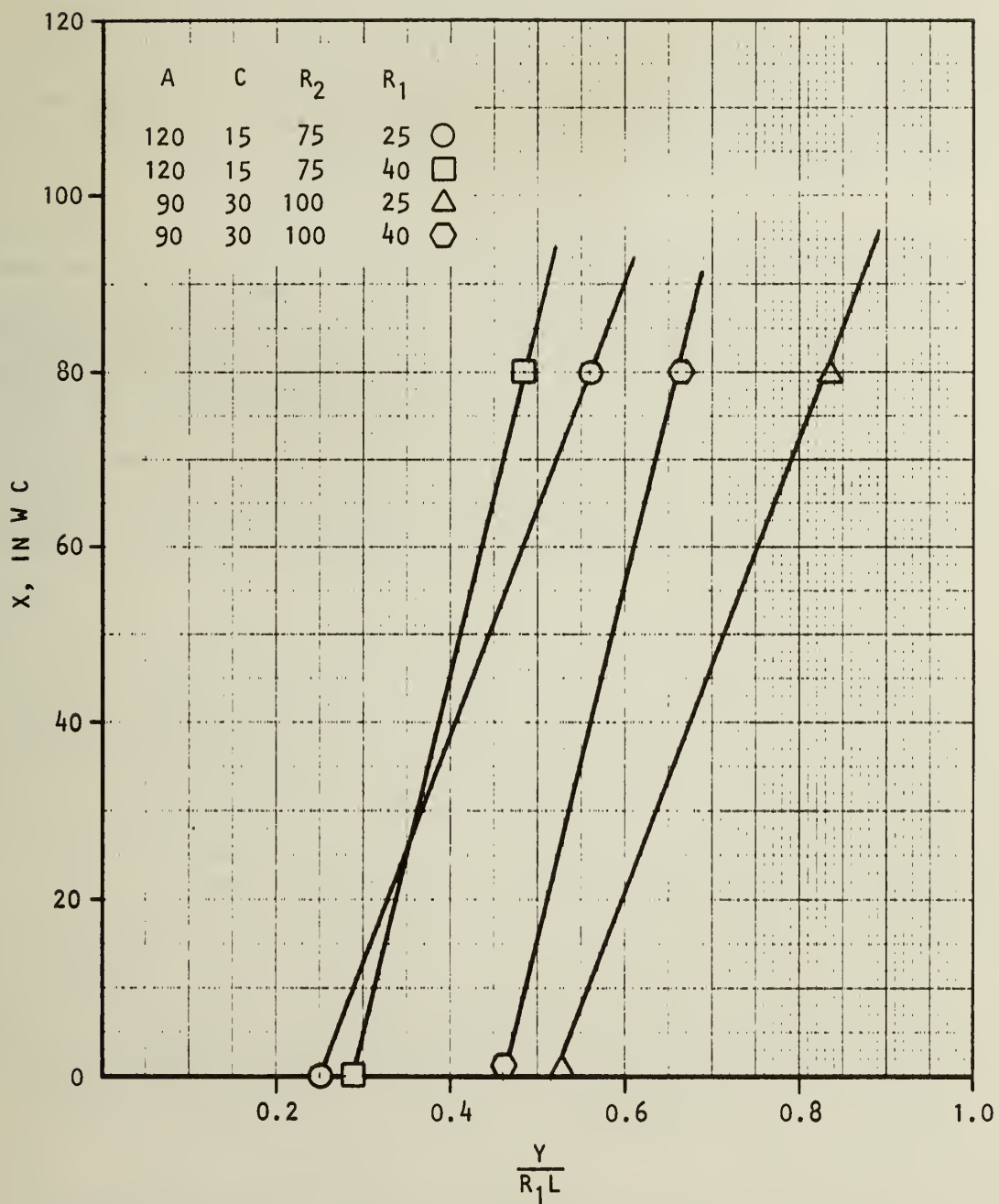
Figure 5-11. CHAR AND LOWER ACCEPTOR STANDLEG DIFFERENTIAL PRESSURE
RELATIONSHIP

63

The lower the pressure drop factor, the less char stripping should take place, due to the lower gas velocity. It is highly desirable, therefore, that the pressure drop factor be kept as low as possible. Since the standleg length (L) is already set by the physical makeup of the plant and the char bed density (R_1) is controlled to meet other process criteria, only the char standleg differential pressure can be lowered to decrease the pressure drop factor. This is accomplished by increasing the differential pressure between the gasifier and the regenerator.

However, Equation 5-19 and Figure 5-11 shows a limit to the lowering of the char standleg differential pressure. If the gasifier-regenerator differential pressure is increased so that the differential pressure across the lower acceptor standleg is zero, there is still a significant differential pressure across the char standleg. It is impossible to operate the pilot plant with zero pressure drop across the char standleg and still maintain a positive differential pressure across the lower acceptor standleg to keep boot steam out of the line. Since dP-2019 on the lower acceptor standleg is operated with a positive differential pressure of 30-60 in. W.C. as a safety factor, the minimum differential pressure across the char standleg is higher still. The minimum differential pressure across the char standleg requires a minimum purge rate on the line. Therefore, some char stripping is unavoidable.

In the pilot plant, the original 2-inch char standleg piping was replaced with 3-inch pipe, and the sloped standleg section was later increased to 4 inches in diameter. Solids plugs did not form as easily in the larger diameter pipe as in the smaller line, because of the reduced tendency for the solids to form bridges across the larger cross-sectional area of the new pipe. The sloped section piping was chosen to be a larger diameter than the vertical section, so that the purge gas velocity would be lower in the sloped section. The lower gas velocity minimized potentially troublesome stripping of fine char in the critical sloped standleg section. Standleg operation was greatly improved by the larger lines.

The value of the term "3.773 R_1" in Equation 5-20, is dependent on the location of the fuel char inlet above the char-acceptor interface level. Thus, the required differential pressure across the char standleg could be lowered if the char withdrawal point on the gasifier was placed lower in the char bed. However, location of the char withdrawal was fixed by the physical design of the pilot plant and could not be changed to benefit the char standleg.

5.2.5.2   Between Vessels

The differential pressure between the gasifier and the regenerator is the overall controlling factor in the system pressure balance. The control of the differential pressure between the vessels is critical; therefore, gross fluctuations in the differential pressure are undesirable.

Maintaining the vessel dP presented several engineering difficulties:

(1)   a 3-6 psi differential between the two large vessels was required, while controlling the gasifier exit pressure at 150 psig.
(2)   Both vessels contained fluidized beds which produced 1 or 2 psi fluctuation in the vessel pressure measurements.

(3) The back-pressure control valves for both vessels are located well downstream of the vessels, with the cyclones, venturis, quench towers, and scrubber towers in between producing a vessel pressure response lag to control valve positioning changes.

(4) Gas flow in the gasifier was peridically subject to wide fluctuations. Changes in coal feed were mostly responsible for this. Any sudden increase in the coal feed rate would cause a sudden gas flow increase as the volatile matter in the coal was rapidly released and gasified. Alternatively, decreasing or stopping coal feed sometimes resulted in a significant drop in reactor gas flow.

Originally, the vessel differential pressure was used to control the regenerator vent control valve, dPCV-2030, so that a constant differential pressure was maintained. This control scheme proved to be ineffective in handling the pressure fluctuations in the two vessels. The system was revised to a cascade control system. This system was installed and operated with good success for the remainder of the pilot plant program.

Under the cascade control system, the pressure in both the gasifier and regenerator is controlled by a pressure control valve on the overhead gas exit line downstream of each vessel. Figure 5-12 shows PCV-2022 and dPCV-2030, pressure control valves for the gasifier and the regenerator, respectively. Each control valve is controlled by the pressure in the respective vessel.

A high pressure in the vessel is sensed by the pressure controller, which signals the pressure control valve to open and vent more gas from the vessel. Low-pressure signals cause the pressure control valve to close and increase the pressure in the vessel. The pressure controller on each vessel is tuned to be fast acting, so that the pressure in each vessel is held roughly constant. The pressure taps for the transmitters are located at the top of each vessel, well out of the fluidized bed, in order to reduce the noise in pressure measurement. Locating the taps in the fluid bed would cause a wider variation in pressure due to the passage of gas bubbles past the taps, and would make control of the vessel pressure much more unstable.

The set point on the gasifier pressure controller, PRC-2022, is manually set at 150 psig. The PCV-2022 valve will respond to correct any deviations in the gasifier pressure from the set point value. The gasifier pressure, therefore, is controlled completely independently of the regenerator pressure and its controller operation.

The set point on the regenerator pressure controller (PRC-2018) is cascade controlled by the vessel differential pressure (dP-2030) signal. If the dP-2030 reading rises above the dPRC-2030 set point level (set normally between 3-6 psi), the signal from dPRC-2030 raises the PRC-2018 set point. Now the PRC-2018 reading is lower than its set point, so the controller sends a signal to close dPCV-2030. The pressure in the regenerator will then rise until it reaches the PRC-2018 set point value.

The dPRC-2030 controller is tuned to be slow acting. In addition, an RC filter is placed in the dPT-2030 signal line to the controller. The RC filter consists of a small valve and tank placed in series in the controller signal line that provides a first-order lag in transmittal of

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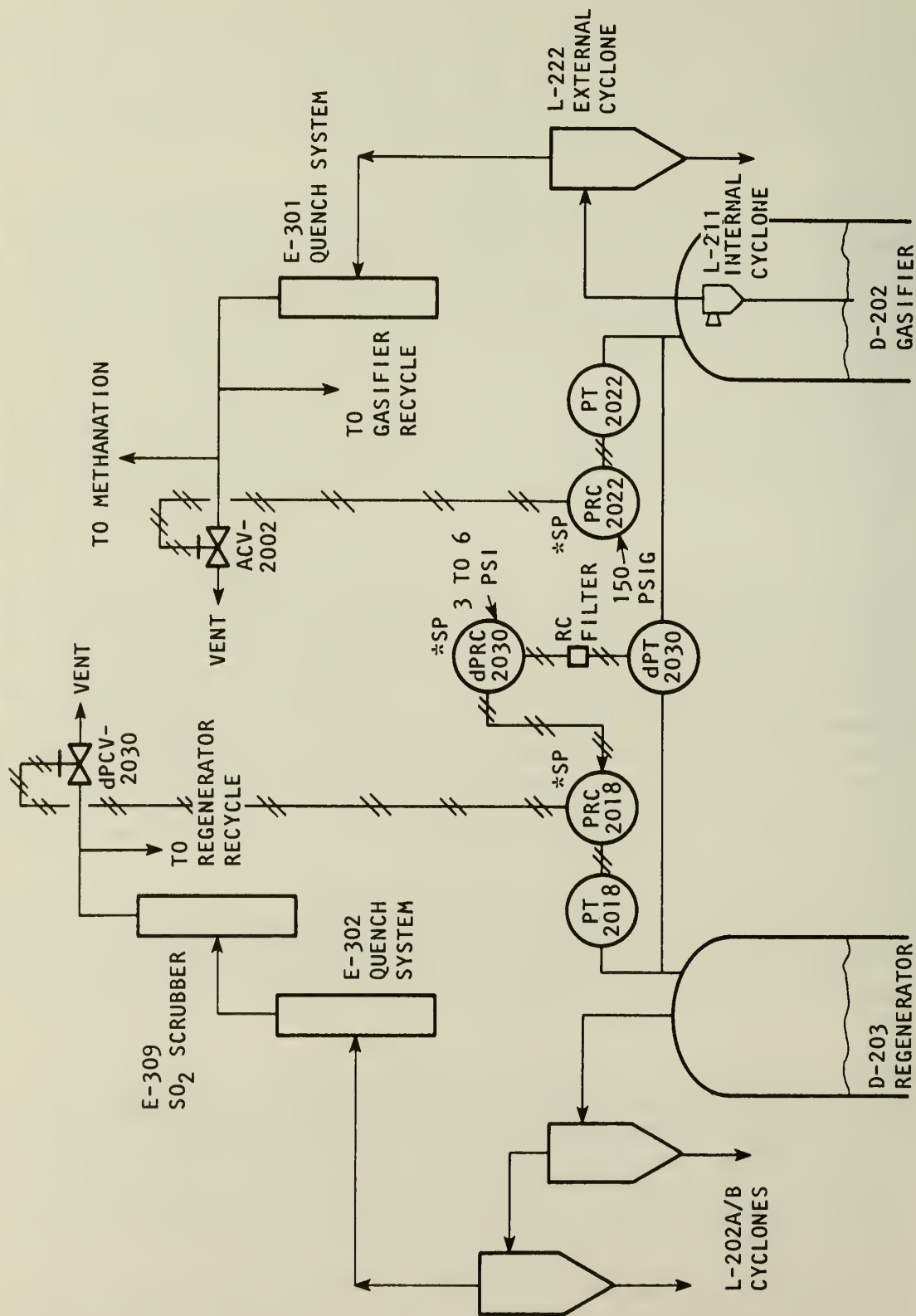
Figure 5-12. VESSEL PRESSURE CONTROL SYSTEM

*SP = SET POINT

66

the pressure signal to the controller. The purpose of the slow-tuned controller and the RC filter is to allow the controlled set point on the regenerator pressure controller, PRC-2018, to follow average fluctuations in dP-2030, rather than the instantaneous differential pressure fluctuations caused by either the regenerator or the gasifier fluidized beds.

Using this cascade control system, the differential pressure between the two vessels can be reliably maintained at a set value. The cascade control method for controlling the regenerator pressure is much better than the original direct control of the regenerator pressure to maintain a constant differential pressure between the vessels. The advantage of cascade control is that pressure fluctuations in either vessel are corrected by the vessel's own fast-acting pressure control system and are not passed on to the other vessel. In the direct control system, the regenerator pressure was forced to follow all gasifier pressure fluctuations. The cascade indirect control of dPCV-2030 allows the valve to follow average (instead of instantaneous) fluctuations in the vessel differential pressure.

3   Across Standlegs

A typical standleg control installation is shown in Figure 5-13. Three such lines are used in the pilot plant to transfer solids between the gasifier and regenerator reactors. The lines are as follows (see Figure 5-10):

(1) The calcined acceptor standleg, CD-206
(2) The recarbonated acceptor standleg, CD-204
(3) The fuel char standleg, CO-202

The solids in the standlegs are not fluidized and are transferred through the lines in a plug flow manner, thereby providing gas seals between the reactors. A balance gas purge is placed on the standleg just above the solids flow control valve in order to prevent process or lift gas from entering the standleg from either end.

The pressure in the standleg is normally highest at the purge injection point and decreases in both directions from that point. This causes the purge gas to flow in both directions from the point of entry, unless influenced by another purge on the standleg. The balance purge therefore controls the pressure drop in the two sections of the standleg.

The sign convention established for the differential pressure in the standleg is that the direction of the overall standleg differential pressure is positive. The pressure drop in the lower section of the standleg across the solids flow control valve is therefore negative. The pressure drop across the upper portion of the standleg, where purge gas flows against the downward moving solids, is positive. The purge gas rate can vary the differential pressure across the two standleg sections, but their sum must always equal the overall standleg differential pressure which is dictated by the differential pressure between the regenerator and gasifier reactors.

The balance gas purge control system is shown in Figure 5-13. The differential pressure across the solids flow control valve regulates the purge flow rate. The purge flow is controlled so that a slightly negative differential pressure across the solids control valve is obtained. The slightly negative differential pressure is maintained, instead of controlling

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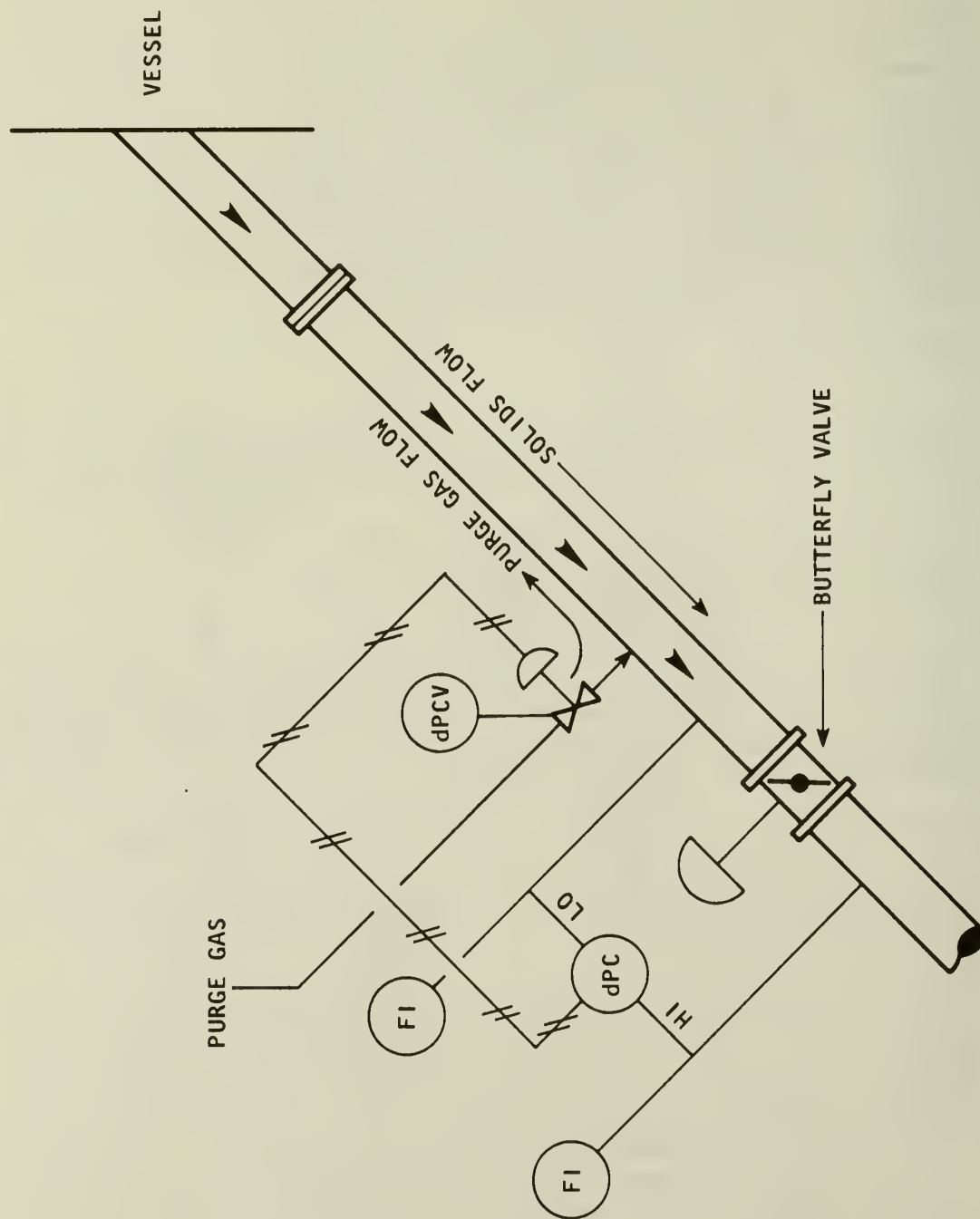
Figure 5-13. SOLIDS TRANSFER LINE

68

at zero pressure differential, as a safety precaution against normal pressure fluctuations in the system which would allow some process gas leakage into the standlegs.

Since the purpose of the purge is to prevent process gas from flowing into the standleg, any additional purge more than that required to just balance the tendency of process gas to enter the line is unnecessary. Furthermore, high-pressure differentials across the solids control valve also increase the purge gas flow up the standleg against the solids flow. This is especially significant in the char standleg, where high upward purge gas flows may lead to char fines stripping and plug formation.

5.3 GASIFIER OPERATION

The heart of the CO_2 acceptor process is the gasifier, in which the endothermic reaction of char and steam must be balanced by the exothermic reaction of calcined acceptor and carbon dioxide to maintain a steady-state operation with regard to pressure, temperature and effluent gas composition.

The achievement of sustained successful gasifier performance requires the following:

(1) Adequate reaction rates.
(2) Control of particle residence times.
(3) Adequate uniformity of particle distribution within the reaction zone.
(4) Effective gas-solids contacting.
(5) Avoidance of conditions resulting in deposits within the system.
(6) Control of solids transport into and out of the vessel, as described in Section 5.2 above.

The following sections present in detail pilot plant results and correlations related to the several factors enumerated above. It is noteworthy that the pilot plant results are consistent with prior bench-scale data[1][2][3] and also with the basis for the design of the projected commercial operation[4]. Accordingly, extrapolation of the pilot plant results to a larger scale of operation can be carried out with confidence.

5.3.1 CO_2 ACCEPTOR PROCESS MODEL

In 1971, Consolidation Coal Co. developed a mathematical model of the CO_2 acceptor process, which was embodied in a computer program, to calculate heat and material balances. The model was continually refined and updated as pilot plant data became available.

(1) Phase II, "Bench-Scale Research on CGS Process - Studies on Mechanics of Fluo-Solids Systems," Jan. 1970, R & D Rpt. No. 16, Interim Rpt. No. 3, Book 1, NTIS: PB-184718/AS.
(2) Phase II, "Bench-Scale Research on CGS Process - Laboratory Physico-Chemical Studies," Jan. 1970, R & D Rpt. No. 16, Interim Rpt. No. 3, Book 2, NTIS: PB-184719/AS.
(3) Phase II, "Bench-Scale Research on CGS Process - Operation of the Bench-Scale Continuous Gasification Unit," Jan. 1970, R & D Rpt. No. 16, Interim Rpt. No. 3, Book 3, NTIS: PB-184720/AS.
(4) "Commercial Plant Conceptual Design and Cost Estimate--CO_2 Acceptor Process Gasification Pilot Plant," DOE Final Report No. FE/1734, Volume 10, Books 1, 2, and 3.

Use of the program requires the following input data:

(1) Gasifier and regenerator bed temperatures.
(2) System pressure.
(3) Coal feed rate and composition.
(4) Gasifier steam and recycle gas flow rates and temperatures.
(5) All purge gas flow rates and compositions.
(6) Regenerator lift gas flow rates and temperatures.
(7) Percent carbon burnout of the regenerator fuel char.
(8) Percent CO in the regenerator dry exit gas.
(9) Acceptor make-up rate.
(10) Acceptor activity.
(11) Heat losses from the gasifier and inlet piping.
(12) Heat losses from the regenerator and inlet piping.
(13) Char loss from the gasifier cyclone, flow rate, and composition.
(14) Methane yield based on correlation of plant and bench scale data.
(15) Regenerator fuel char composition (% H, N, S).
(16) Regenerator auxiliary fuel flow rate and composition.

The program generates the following output data:

(1) Flow rates and compositions of the outlet gas streams.
(2) Enthalpies of all streams, inlet and outlet.
(3) Acceptor circulation rate.
(4) Regenerator fuel char flow rate, % C, % ash.
(5) Regenerator air inlet rate.
(6) Regenerator overhead char + ash, flow rate, and composition.
(7) Purged acceptor flow rate.
(8) ΔP CO_2 driving forces in the gasifier and regenerator.
(9) Kinetics data for rate of fixed carbon gasification.
(10) Yields of H_2S and NH_3* based on plant and bench-scale data.

Calculations of accurate heat and material balances strictly from plant data are hindered by the lack of the following data:

(1) Because of the severe pressure and temperature conditions, the acceptor circulation rate and regenerator fuel char rate cannot be measured directly. This problem was recognized during the design of the plant, and the decision was made to calculate these rates by means of heat and material balances. This need was the prime motivation to develop the mathematical model of the plant.

(2) At times, some of the desired measurements of flows, compositions, etc., cannot be made because of mechanical problems.

The model internally closes the heat balances and the elemental and ash balances for each reactor to within 1 part per million. Data in the tables in Section 5.6 will show very slight gaps which are caused by rounding. A cornerstone of the model is that water gas shift equilbrium occurs, an assumption which has been confirmed in the CCDC laboratories over many years in experiments with several coal-based systems.

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* The NH_3 yield is taken as 60% of the coal nitrogen, based on bench-scale data.

Standard conditions are:

(1) 60° F.
(2) Liquid water.
(3) 1 pound mol = 379 standard cubic feet.

The heat balances and the elemental balances for C, H, O, and S, as well as the ash balances for each reactor, are embodied in a set of 19 nonlinear simultaneous equations which are solved by an iterative technique.

5.3.2 METHANE YIELD CORRELATION

5.3.2.1 Introduction

During Radian Corporation sampling of the gasifier product gas upstream of the quench tower (see Volume 11 of this report), the only hydrocarbons other than methane which were found in amounts above the practical limits of detectability were:

		Concentration, ppmv in dry gas
(1)	C_2H_4 + C_2H_6	390
(2)	Benzene	150
(3)	Naphthalene	2-5

In the CO_2 acceptor process model, in view of the above low concentrations, the assumption is made that the only hydrocarbon in the raw product gas is methane.

In conjunction with elemental balances for C, H, and O, along with the assumption of equilibrium in the water gas shift reaction, the product gas composition can be calculated if the methane yield can be specified.

5.3.2.2 Correlation for Lignite and Bituminous Coal Chars

In 1972, Consolidation Coal Company obtained kinetics data on the rate of fixed carbon gasification of a bituminous coal char.[5] A continuously fed fluidized bed reactor was used at 15 atm abs pressure. Data from that study which are pertinent to the discussion here are shown in the first two sections of Table 5-2. Subsequent to the publication of the cited work, a correlation was developed which expressed the amount of methane formed as functions of the partial pressures of the other components in the outlet gas.

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(5) Curran, G. P. et al, "Production of Clean Fuel Gas from Bituminous Coal,: Work Sponsored by EPA Under Contract No. EHSD71-15, Dec. 1973, NTIS: PB-232695/AS.

$$P_{CH_4} = A \left(P_{H_2}\right)^B \left(P_{CO_2}\right)^C \qquad \text{(Equation } \underline{5\text{-}21}\text{)}$$

p = partial pressure, atmospheres

A = exp (-241.321 + .0558481T + 254651/T)

B = exp (.943958 - .000557601T + 1090.12/T)

C = exp (14.0442 - 33604.6/T)

T = °R = °F + 460

Data Used For Correlation[5, **]
Bituminous Coal Char
1820°F

Run	P_{H_2}	P_{CO}	P_{CO_2}	P_{H_2O}	P_{Inert} *	Obs. P_{CH_4}	Calc. P_{CH_4}	% Diff.
K1	2.178	1.467	1.278	2.390	7.563	.128	.127	.8
K2	3.490	1.288	1.042	3.564	5.393	.223	.236	5.8
K3	2.111	2.113	3.925	4.947	1.761	.143	.140	-2.1
K4	3.475	1.449	1.847	5.598	2.361	.270	.252	-6.7
K5	2.718	1.583	2.920	6.326	1.243	.210	.190	-9.5
K6	5.040	.476	.387	4.906	3.839	.372	.343	-7.8
K7	2.567	.809	1.032	4.133	8.274	.185	.155	-16.2
K2A	2.800	1.215	1.270	3.700	5.857	.158	.179	13.3
K4A	3.465	1.393	1.892	5.946	2.050	.254	.252	-.8
K5A	2.618	1.439	2.948	6.771	1.055	.168	.181	7.7
K6A	4.972	.378	.308	5.113	3.812	.317	.330	4.1
K7A	2.300	.560	1.004	5.205	5.787	.134	.133	-.7
							Mean	6.3
							Standard Deviation	4.8
max/min	2.4	5.6	13	2.8	7.2	3.0		

1700°F

Run	P_{H_2}	P_{CO}	P_{CO_2}	P_{H_2O}	P_{Inert} *	Obs. P_{CH_4}	Calc. P_{CH_4}	% Diff.
K10	2.181	2.230	1.260	1.787	7.483	.099	.112	13.1
K11	3.404	2.065	1.006	2.375	5.869	.181	.188	4.4
K12	2.005	3.296	4.078	3.563	1.902	.155	.131	-15.5
K13	4.313	2.277	1.556	4.230	2.350	.274	.281	2.6
K14	3.161	2.807	2.871	4.641	1.315	.205	.217	5.8
K15	6.022	.868	.341	3.401	4.022	.348	.308	-11.5
K16	3.216	1.501	.864	2.959	6.218	.142	.174	22.5
K11A	3.386	1.883	1.014	2.613	5.824	.174	.188	8.0
K12A	1.773	3.060	4.315	3.588	2.127	.137	.113	-17.5
K13A	4.011	2.158	1.868	4.451	2.457	.255	.260	2.0
K14A	3.038	2.599	2.983	4.999	1.188	.182	.208	14.3
K15A	5.864	.648	.264	3.495	4.305	.328	.288	-11.6
							Mean	10.7
							Standard Deviation	8.1
max/min	3.4	5.1	16	2.8	5.0	3.5		

CO₂ Acceptor Pilot Plant Data
Lignite Char

← ———— Data Calculated from Tables 5-13 through 5-24 ————→

Run	Bed Temperature, °F	P_{H_2}	P_{CO}	P_{CO_2}	P_{H_2O}	P_{Inert} *	Calc.[1] P_{CH_4}	Calc.[2] P_{CH_4}	Obs.[3] P_{CH_4}	100 ([2] - Obs.) / Obs. % Diff.
21-I	1480	4.478	1.187	.622	3.083	.300	1.139	1.197	1.172	2.1
21-II	1480	4.490	1.135	.808	3.138	.295	1.136	1.201	1.222	-1.7
21-III	1500	4.208	1.315	.838	2.728	1.082	.830	.838	.950	-12.0
28B	1495	5.001	1.254	.873	2.708	.278	1.088	1.145	1.211	-5.4
28B	1490	4.818	1.400	.847	2.795	.280	1.059	1.095	1.132	-3.3
33B	1490	4.858	1.368	.825	2.811	.277	1.083	1.108	1.094	1.3
38	1490	4.888	1.281	.881	2.603	.451	1.085	1.187	1.088	6.0
40B	1480	3.648	1.235	.881	2.551	1.738	.948	.878	.838	-6.6
46C	1490	5.385	1.883	1.160	3.690	.882	1.290	1.400	1.298	8.0
47B	1510	4.828	1.817	.758	2.353	.500	.943	.904	.888	-8.3
					Mean of 34 Data Sets 7.7%				Mean	5.7
					Standard Deviation 5.4%				Standard Deviation	3.3

(1) Loosely converged. See text.
(2) Calculated from Equation 5-21.
(3) Calculated from plant dry gas CH₄ contents and outlet wet gas flowrates from Tables 5-13 through 5-24.

* P_{Inert} is the partial pressure of N₂ plus small amounts of H₂S and NH₃.

References

(5) Curran, G. P., et al, "Production of Clean Fuel Gas from Bituminous Coal." December, 1973, NTIS PB-232-885/AS. Work sponsored by EPA under Contract No. EHSD 71-15.

(**) This work.

Table 5-2. METHANE YIELD CORRELATION

As data became available from the CO_2 acceptor pilot plant, this cor-
relation (with slight modification) was incorporated into the process
model and was found to predict very well the observed yields of
methane for the runs in which lignite char was fasified. The modified
correlation was used from 1975 to 1977. After the final workup of
the pilot plant data, a new correlation was developed which included
the ten sets of lignite data selected for calculation of the detailed
heat and material balances which are presented in Subsection 5.3.6.
Data which are pertinent to the correlation are shown in the third
section of Table 5-2.

The correlation expresses the methane partial pressure at the top of
the gasifier bed as functions of the H_2 and CO_2 partial pressures and
the bed temperature:

$$P_{CH_4} = A(pH_2)^B (pCO_2)^C \qquad\qquad (5-21)$$

p = partial pressure, atmospheres
A = exp. (-241.321 + .0556461T + 254651/T)
B = exp. (.943958 - .000557601T + 1090.12/T)
C = exp. (14.0442 - 33604.6/T)
$T = {}^{\circ}R = {}^{\circ}F + 460$

The methane yield correlation was not part of the original computerized
version of the process model. Incorporation of the correlation into the
matrix which expresses 19 nonlinear simultaneous equations would have
required a major revision of the original computer program. Instead,
a simple subroutine was added which allowed convergence of the methane
yield by using trial values of the methane content of the dry product
gas. In use of the program, the methane yield was not tightly con-
verged. To have done so would have approximately doubled the computer
time charges. Table 5-2 shows two columns of calculated methane partial
pressures for the pilot plant runs. The mean difference between the
loosely converged values and those calculated from Equation 5-21 is 5%
with a maximum difference of 9%.

5.3.2.3 Correlation for Subbituminous Coal Char

Equation 5-21 does not predict very well the pilot plant methane yields
in the four subbituminous coal runs selected for calculation of the detailed
heat and material balances presented in Section 5.3.6.

In coal rank, subbituminous coal lies between lignite and bituminous coal.
On the assumption that the exponents, B and C, in Equation 5-21 are in-
dependent of rank, the coefficient, A, in Equation 5-21 was calculated
for each run from the data given in Table 5-3. The mean value of A was
0.1112 and the individual values showed no trend with bed temperature.
The methane yield correlation for subbituminous coal char then becomes,

$$P_{CH_4} = .1112 \ (pH_2)^B (pCO_2)^C, \qquad\qquad (5-22)$$

with the terms defined as previously. As shown in Table 5-3, the mean
deviation of the calculated methane partial pressure is 3.5%.

The lack of temperature dependence for A probably is the result of
assuming the B and C are independent of coal rank. Not enough data are
available from plant operations to evaluate the individual temperature
dependencies of A, B, and C.

73

$$P_{CH_4} = .1112 \left(P_{H_2}\right)^B \left(P_{CO_2}\right)^C \qquad \text{(Equation } 5\text{-}22 \text{)}$$

Data Calculated from Tables 5-11, 5-12, 5-19, and 5-22 →

Run	Bed Temperature, °F	P_{H_2}	P_{CO}	P_{CO_2}	P_{H_2O}	P_{Inert}	Obs. (1) P_{CH_4}	Calc. (2) P_{CH_4}	% Diff.
31-III	1480	2.531	1.509	1.326	2.180	3.090	.464	.465	.2
31-II	1470	2.569	1.580	1.338	2.089	3.023	.501	.481	-4.0
38C	1515	4.268	1.113	.699	2.836	1.120	.964	.940	-2.5
45	1528	4.586	1.406	.814	2.870	.365	.959	1.028	7.2
								Mean	3.5

(1) Calculated from plant dry gas CH_4 content and wet gas flowrates given in Tables 5-11, 5-12, 5-19, and 5-22 .
(2) Calculated from Equation 5-22 .

Table 5-3. METHANE YIELD CORRELATION FOR SUBBITUMINOUS COAL CHAR

5.3.3 GASIFICATION KINETICS MODEL FOR LOW-RANK COAL CHARS

5.3.3.1 Introduction

In 1966, Consolidation Coal Company made a detailed study of the [6] kinetics of fixed carbon gasification of a lignite char at $1500°F$. A batch fluidized bed reactor system was used at a total pressure of about 16 atm abs. Special emphasis was placed on measuring accurately the rate of CH_4 formation. The data were correlated on the basis of the following model reactions:

(1) $C + H_2O = CO + H_2$ (for carbon oxides formation)

(2) $2 C + H_2O + H_2 = CH_4 + CO$ (for methane formation)
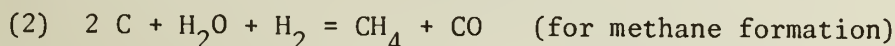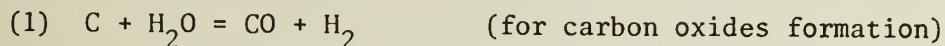
Attainment of water gas shift equilibrium was demonstrated conclusively, even in fluidized beds containing as little as one gram each of carbon and ash with a nominal gas contact time of 1 second.

The following rate expressions were developed.

$$R_c = \frac{k(p_{H_2O} - p_{CO}p_{H_2}/K)}{(1 + K_1 p_{H_2O} + K_2 p_{H_2} + K_3 p_{CO})^2} \qquad (5-23)$$

$$R_{CH_4} = \frac{k'(p_{H_2O}p_{H_2} - p_{CH_4}p_{CO}/K')}{(1 + K'_1 p_{H_2O} + K'_2 p_{H_2} + K'_3 p_{CO} + K'_4 p_{CH_4})^2} \qquad (5-24)$$

$$R_c = R_T - 2 R_{CH_4} \qquad (5-25)$$

where:
p = partial pressure, atm

$$R_T = \frac{\text{lb carbon in } (CO + CO_2 + CH_4) \text{ formed/minute} \times 10^4}{\text{lb fixed carbon in bed}}$$

$$R_{CH_4} = \frac{\text{lb carbon in } CH_4 \text{ formed/minute} \times 10^4}{\text{lb fixed carbon in bed}}$$

k, K, etc = experimentally determined constants

The carbon oxides rate, R_c, is given by $R_T - 2R_{CH_4}$ because one mol of CO accompanies each mol of CH_4 according to the model reaction for CH_4 formation.

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(6) Curran, G. P. et al, "Kinetics of Lignite Char Gasification," I & EC Process Design and Development, Vol. 8, Oct, 1969, p. 559.

75

Later, additional kinetics data for lignite char gasification were obtained in a continuously fed fluidized bed reactor at temperatures of $1500°F$ and $1600°F$[3]. System pressures were 11 and 20 atm abs. The data were correlated by using Equations 5-23 and 5-24. To allow direct use of these equations, the assumption was made that an "effective" gas composition could be assigned to each set of experimental data. Somewhat arbitrarily, the effective gas compositions were taken as 90% of the outlet gas partial pressures + 10% of the inlet gas partial pressures. The assumption appeared to be justified, because very good correlations were obtained. As in the batch data correlation, the value of K' in Equation 5-24 was taken as the equilibrium constant for the reaction,

$$2\ C_{gr} + H_2O + H_2 = CH_4 + CO$$
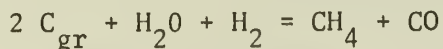
$$C_{gr} = \text{graphite}$$

Results of the study gave the following temperature dependent expressions for the constants in Equations 5-23 and 5-24.

$$k = 1615 \exp(44.096 - 90840/T) \tag{5-26}$$
$$K = 18.52 \exp(29.179 - 60110/T) \tag{5-27}$$
$$K_1 = .05 \exp(31.548 - 64990/T) \tag{5-28}$$
$$K_2 = .20 \tag{5-29}$$
$$K_3 = 1.4 \exp(10.738 - 22120/T) \tag{5-30}$$
$$k' = 41.8 \exp(39.587 - 81550/T) \tag{5-31}$$
$$K' = .491 \exp(4.6053 - 9487/T) \cdot \tag{5-32}$$
$$K'_1 = .05 \exp(9.995 - 20590/T) \tag{5-33}$$
$$K'_2 = .15 \exp(-19.204 + 39560/T) \tag{5-34}$$
$$K'_3 = 1.4 \exp(9.7766 - 20140/T) \tag{5-35}$$
$$K'_4 = .7 \exp(11.1700 - 23010/T) \tag{5-36}$$

$$T = °R = °F + 460$$

5.3.3.2   The Kinetics Model - Application of Rate Equations to the CO_2 Acceptor Process Gasifier

Dry coal is fed to the bottom of the gasifier where it is devolatilized rapidly.[7] The rate of gasification of the residual fixed carbon is slow, compared with the devolatilization rate. To use the kinetics model for prediction of the overall rate of fixed carbon gasification, the conditions at the bottom of the gasifier must be defined. The following set of assumptions are made to provide the partial pressures of the gas components leaving the top of an hypothetical zone, termed "Zone zero," which conceptually is very thin compared with the height of the gasifier fluidized bed.

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(3)   Phase II, "Bench-Scale Research on CSG Process - Operation of the Bench-Scale Continous Gasification Unit," January, 1970. Interim Rpt. No. 3, Book 3, Research and Development Report No. 16, National Technical Information Service PB-184720/AS.

(7)   Suuberg, E. M. et al, "Product Composition and Kinetics of Lignite Pyrolysis", I & EC Process Design and Development, Vol. 17, January, 1978, p.37.

(1) All of the coal oxygen is released.

(2) All of the product H_2S and NH_3 are formed in the zone.

(3) All of the purge gas streams enter the zone.

(4) All of the coal hydrogen except that contained in the char streams leaving the gasifier is released.

(5) All of the volatile carbon in the coal is released. The volatile carbon content is obtained for each feedstock by a laboratory assay in which a sample of dry coal, fluidized in H_2, is heated rapidly to 1500°F by being immersed suddenly into a fluidized sand bath furnace preheated to 1510°F. Typically, the volatile carbon is about 25% of the total carbon in the coals which were used.

(6) No fixed carbon is gasified in the zone.

(7) All of the acceptor $CaCO_3$ is formed above the zone.

(8) Water gas shift equilibrium is attained.

(9) The methane content of the gas leaving the zone is that given by the methane yield correlation described in Subsection 5.3.2.

With these assumptions, along with the known flow rates of coal and steam entering the gasifier,* the gas composition and component partial pressures leaving the zone are calculated through use of elemental balances for carbon, hydrogen, and oxygen. No assumption as to the nature of gas-solids contacting is needed to carry out this calculation.

The remainder of the kinetics model is constructed as follows, with use of the gasifier output data from the process model such as are shown in Subsection 5.3.6 (Heat and Material Balances).

(1) The amount of fixed carbon gasified is defined as: total carbon in - (volatile carbon released in Zone zero + carbon in all char streams leaving the gasifier).

(2) The amount of methane leaving the top of the gasifier bed is determined by the process model which uses the methane yield correlation described in Subsection 5.3.2.

(3) The gasifier bed is divided into four zones, in each of which the following occurs.

    (a) One-fourth of the fixed carbon gasification occurs.
    (b) One-fourth of the difference between the methane leaving the top of the gasifier and that leaving Zone 0 (entering Zone 1) is added to the gas which enters the zone.

* If air, recycle gas, or CO_2 are fed to the gasifier as an adjunct to operations, these flow rates are included.

(c) One-fourth of the total $CaCO_3$, including the small amount present in the char ash streams, is formed.

(d) Water gas shift equilibrium is attained.

(e) As in Zone 0, no assumptions about gas-solids contacting are made.

(4) The gas compositions and component partial pressures leaving each zone are calculated through use of carbon, hydrogen, and oxygen balances.

(5) As was done for the correlation of the earlier continuous unit kinetics data, an effective partial pressure for the components in each zone was assigned by taking 90% of the outlet gas partial pressures plus 10% of the inlet gas partial pressures.

(6) Using the effective partial pressures, Equations 5-23, 5-24, and 5-25 are solved for each zone.

(7) Since an equal amount of fixed carbon is gasified in each zone, the overall gasificiation rate, R_T, is given by:

$$4/R_T = 1/R_{T_1} + 1/R_{T_2} + 1/R_{T_3} + 1/R_{T_4} \qquad (5-37)$$

5.3.3.3   Kinetics of Fixed Carbon Gasification for Subbituminous Coal Char

During the study[3] which provided kinetics expressions for gasification of lignite char, five runs were made with subbituminous coal char at $1600°F$. Unfortunately, only a single run was made at $1500°F$. Therefore, development of kinetics expressions covering a range of temperatures was not possible.

Runs 38C and 45 at the pilot plant gave the opportunity to develop the needed kinetics expressions for subbituminous coal char. A stepwise procedure was required to use the plant data, which gave only the total gasification rate, R_T, to provide temperature dependent expressions for R_c and R_{CH_4}. A necessary assumption was made that the coefficients in the denominators of Equations 5-23 and 5-24 are the same for both subbituminous coal and lignite chars.

5.3.3.3.1 Recorrelation of the Earlier $1600°F$ Data

With the above assumption, the new values of k and K in Equations 5-23 and 5-24 for R_c and R_{CH_4} are:

k = 790   k' = 16.83
K = 13.96   K' = .491

Comparisons of the correlated and measured values of R_c and R_{CH_4} are shown below.

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(3) Phase II, "Bench-Scale Research on CGS Process - Operation of the Bench-Scale Continuous Gasification Unit," Jan. 1970, R & D Rpt. No. 16, Interim Rpt. No. 3, Book 3, NTIS: PB-184720/AS.

	R_c			R_{CH_4}		
Run	Calc.	Obs.	% Diff.	Calc.	Obs.	% Diff.
K3E	25.7	22.5	14.2	5.07	5.7	-11.0
K3B	27.2	27.4	-.7	6.24	6.2	.6
K3F	33.7	33.7	0	8.23	7.8	5.5
K3D	52.0	54.8	-5.1	5.06	5.7	-11.2
K2	21.9	23.8	-8.0	9.18	7.4	24.0
		Mean	5.6			10.5

5.3.3.3.2 Calculation of k' vs. Temperature Expression Using Pilot Plant Data

A further assumption had to be made here in that the rate, R_{CH_4}, in Equation 5-24 for the plant data was in proportion to the ratio,

$$\frac{\text{Measured } R_T \text{ from plant data}}{R_T \text{ from plant partial pressures* calculated as if lignite char were used}}$$

Data from a preliminary workup of Run 38C were used in the process model to supply the needed partial pressures. The coefficient, k', then was calculated from Equation 5-24 and was corrected by the above ratio, giving the value of 3.462 at $1515^{\circ}F$. This, in conjunction with the $1600^{\circ}F$ value, gave the following temperature dependent expression.

$$k' = 16.83 \exp(36.7409 - 75686.3/T) \tag{5-38}$$

5.3.3.3.3 Calculation of K vs. Temperature Expression Using Pilot Plant Data

In Equation 5-23, the coefficients k and K, cannot be deduced from plant data as simply as was k' in Equation 5-24. The temperature dependency of neither k nor K is known. (The temperature dependency of K' in Equation 5-23 is known, because it had been defined as the equilibrium constant for the reaction, $2 C_{gr} + H_2O + H_2 = CH_4 + CO$.)

Equation 5-23 can be rearranged as:

$$P_{H_2O} = \frac{P_{CO}P_{H_2}}{K} + \frac{R_c(\text{denominator})}{k}$$

Data from preliminary workups of Run 38C and 45 were used in the process model to supply the necessary partial pressures for use in developing a preliminary kinetics expression for R_c. The kinetics model also was used to provide the outlet partial pressures from Zone 3. These partial pressures, along with the gas partial pressures at the top of the gasifier, gave four sets of input data for the above equation, which was solved for k and K using a least squares technique. The values of R_c had been multiplied by the same ratio used in 5.3.3.3.2, above. The resulting preliminary value of k, 119.5 at $1522^{\circ}F$**, in conjunction with the $1600^{\circ}F$ value, gave the following temperature dependent equation:

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* Partial pressures at the top of the gasifier bed were used.
** The mean temperature for Runs 38C and 45 ($1515^{\circ}F$ and $1528^{\circ}F$, respectively).

79

$$k = 790 \exp(47.9927 - 98861/T) \qquad (5-39)$$

Next, the value of K was calculated from the single set of data at $1500°F$ obtained in the previous work.[3] The value of k at $1500°F$ from Equation 5-39, 68.41, was used in Equation 5-23 for the calculation. The resulting value, 4.136, in conjunction with the $1600°$ value, gave the following temperature dependent equation:

$$K = 13.96 \exp(23.8428 - 49116.1/T) \qquad (5-40)$$

The equation for K was formulated in this manner in order to give more weight to the pilot plant data in determining the equation for k, as described in the next section. Experience with the kinetics model shows that at CO_2 acceptor process conditions the reaction rate is more sensitive to the value of k than to that of K.

5.3.3.3.4 Calculation of k vs. Temperature Expression Using Pilot Plant Data

Data from the final workup of Run 38C were used in the process model to supply the necessary partial pressures. The entire four-zone model was used, which contained the values for k' and K just obtained, leaving only the value of k to be determined. The values of R_c from Equation 5-23 were calculated using the lignite char coefficients and were multiplied by a factor, F. The model calculations were repeated, using trial values of F, until the calculated R_T matched the measured R_T from the plant data. The value of k then was calculated from Equation 5-23, with F x R_c being substituted for R_c. The resulting value of k, 82.41 at $1515°F$, in conjunction with the $1600°F$ value, gave the following temperature dependent equation:

$$k = 790 \exp(52.5194 - 108190/T) \qquad (5-41)$$

The procedure purposefully avoided use of the final data workup for Run 45, although preliminary Run 45 data were used in developing the expression for K in 5.3.3.3.3, above. At the time this work was done, the final data workup for Run 45 was not available, and the intent was to use these data as a test of the validity of the assumptions which had to be made.

In Run 45, the partial pressures were appreciably different from those in Run 38C. Thus, the run data provide a fairly severe test of the rate expression for subbituminous coal char. The comparison is shown below:

R_T		
Plant	Correlation	% Diff.
48.7	47.6	-2.2

The new equations for use in Equations 5-23 and 5-24 for subbituminous coal char are tabulated below:

$$k' = 16.83 \exp(36.7409 - 75686.3/T) \qquad (5-38)$$
$$K = 13.96 \exp(23.8428 - 49116.1/T) \qquad (5-40)$$
$$k = 790 \exp(52.5194 - 108190/T) \qquad (5-41)$$
$$T = °R = °F + 460$$

5.3.3.4 Comparison With Pilot Plant Kinetics Data

The overall gasification rate from pilot plant data is determined as follows. Data from Run 28B are used as an example. The pertinent data are taken from Tables 13-31, Appendices Subsection 13.4, of Volume 12, Book 4 and Table 5-17 in Volume 12, Book 2, and from Table 28-20 in Volume 8, Book 4. The Velva lignite which was used contains 16 lb volatile carbon/100 lb dry feed coal.

5.3.3.4.1 Fixed Carbon Gasified

Let N = lb/hr fixed carbon gasified. Then, by the definition of fixed carbon gasified given in Subsection 5.3.3.2.

$$N = 2570 \ (.6673) - \left[2570(.16) + (537 + 114)(.7557) + 122(.6920) \right] = 727 \text{ lb/hr}$$

5.3.3.4.2 Inventory of Fixed Carbon in the Gasifier

(1) The pressure drop across the gasifier bed is calculated from the mean value of the last three entries for Location 3 in Table 28-20, Volume 8, Book 4. This value (154.6 inches H_2O) is equivalent to 803 lb/ft^2. This pressure drop multiplied by the reactor cross sectional area (8.72 ft^2) gives 7002 lb total inventory.

(2) The weight fraction char in the bed is given as .516 in Table 13-31, Appendices Subsection 13.4 of Book 4.

(3) The weight fraction carbon in the bed is assumed to be the same as that in the fuel char which goes to the regenerator and which is given in Table 5-17 as .7557.

(4) Let W = lb fixed carbon inventory. Then, W = 7002(.516)(.7557) = 2730 lb.

5.3.3.4.3 Overall Gasification Rate

$$R_T = \frac{N \times 10^4}{W(60)} = \frac{727 \times 10^4}{2730(60)} = 44.3$$

5.3.3.5 Results and Discussion

Table 5-4 shows a comparison of the measured plant overall gasification rates with those predicted by the kinetics model. Some pertinent conditions also are shown for the runs which used lignite as the feedstock. The mean difference between the measured and predicted rates is 4.8%. In view of the many assumptions which were made in constructing the kinetics model the agreement is very good.

Run	Bed Temperature, °F	Coal Feedrate lb/hr	Mols Steam/ 100 lb coal	% Steam Conversion	Lb/hr FC Gasified	Inventory, lb FC	R_T Plant	R_T Model	% Diff.	Mols Recycle Gas/ mols steam (3)	R_T Bottom (c)	R_T Top (c)	R_T Bottom/ R_T Top
21-I	1480	2550	6.11	50.4	656	2460	44.4	42.4	-4.6	.20	112	22.6	5.0
21-II	1480	2600	6.07	49.0	652	2520	43.1	44.2	2.6	.21	112	24.2	4.6
21-III	1500	2500	5.55	50.9	648	1575	68.6	65.6	-4.4	.16	203	33.2	6.1
26B	1495	2450	5.92	55.3	660	2480	44.4	46.8	5.4	.26	145	22.7	6.4
28B	1490	2570	5.54	58.6	727	2730	44.3	44.1	-.5	0	183	18.2	10.1
33B[2]	1490	2770	5.37	58.0	754	2750	45.7	45.4	-.6	0	181	19.2	9.5
39[1]	1490	2690	5.45	59.0	699	2740	42.5	38.3	-9.9	.19	140	16.5	8.5
40B[a]	1480	2530	5.14	51.5	646	2430	44.3	39.8	-10.2	.18	129	18.8	6.9
								Mean	4.8				

(1) Glenharold lignite.⎤ others are Velva lignite
(2) Texas lignite.⎦
(a) Entering bottom of gasifier.
(c) Reaction rates corresponding to the partial pressures of the gases entering Zone 1 and leaving Zone 4.

Table 5-4. COMPARISON OF OVERALL GASIFICATION RATES FOR LIGNITE CHAR PILOT PLANT VS. KINETICS MODEL.

The measured rates indicated that the Glenharold and Texas lignite char are slightly more reactive than is the Velva lignite char. Kinetics comparisons for two other lignite runs for which heat and material balance data are given in Subsection 5.3.6 are not shown in Table 5-4 because mechanical problems had occurred during these runs.

Run 46C - the boot steam flow recorder malfunctioned during the balance period.

Run 47B - A large leak at the boot steam flow control valve downstream of the measuring orifice occurred early in the run. It could not be repaired while the plant was in operation.

In view of the excellent agreement between the predicted and measured overall gasification rates for the other lignite runs, the "missing" steam flows were supplied by using trial values in the process model until the measured plant gasification rates matched the predicted rates to within ± 1 rate unit.

The reaction rates are inhibited severely by the reaction products, H_2, CO, and CH_4. The rates also are decreased by the consumption of steam as the gases move upward through the gasifier. As shown in the right-hand column of Table 5-4, for the runs in which no recycle gas was used, the gasification rate decreases by a factor of about 10 in going from the bottom to the top of the gasifier. Recycle gas was used in the other runs for reasons given in Subsection 5.3.6. In these runs, presence of the inhibitors in the recycle gas decreased the rate at the bottom relative to that at the top.

Table 5-5 shows how the total gasification rate, R_T, varies with temperature for both lignite and subbituminous coal chars. The overall gasification rate from the 4 Zone kinetics model (see Equation 5-37) corresponds most closely with the rate in Zone 3. The partial pressures shown in the Table are those from the Zone 3 calculations for Run 28B, taken to be representative of plant operations when no air or recycle gas were fed to the gasifier. In the range of temperatures used in the CO_2 acceptor process, R_T doubles with each 26°F increase in gasifier temperature for lignite char and with a 24° increase for subbituminous coal char. At the given partial pressures, R_T is about three times greater at the same temperature for lignite char than for subbituminous coal char. To compensate for the lower reactivity of subbituminous coal char, the temperature must be increased. As the right-hand column of the Table shows, a temperature increase of about 40°F is needed to give the same gasification rate as for lignite char. Compensation also can be accomplished by increasing the ratio of steam/coal fed to the gasifier and then operating at lower temperatures than are shown in the Table.

5.3.3.6   Comparison With Measurements Made at the Bottom of the Gasifier

During Run 47B, gas compositions at three levels in the bottom of the gasifier were obtained as described in Subsection 5.3.4. This body of data was used to test the validity of the kinetics model.

The model was constructed on the assumption that a thin zone exists at the bottom of the gasifier in which only the very rapid devolatilization reactions occur. In reality, an appreciable volume exists below the coal feed point in which fixed carbon is present (see Figure 5-14).

83

Partial Pressure, atm

H_2O	3.56
H_2	4.04
CO	1.23
CH_4	.82

Mols Steam/100 lb dry coal = 5.54

°F	R_T Lignite	R_T Subbituminous	R_T Lignite/R_T Subbituminous	Equivalent Temperature, °F[1]
1480	32.0	10.5	3.05	1518
1490	43.6	14.4	3.03	1530
1500	57.8	19.5	2.96	1541
1510	74.9	25.9	2.89	1552
1520	95.3	33.9	2.81	[2]
1530	119.7	43.9	2.73	[2]

(1) Temperature needed for subbituminous coal char to give same gasification rate as for lignite.
(2) Unrealistic because the CO_2 partial pressure at the top of the gasifier bed would be too low to recarbonate the acceptor.

Table 5-5. EFFECTS OF TEMPERATURE ON GASIFICATION RATES

For comparison with the experimental data, the 4-zone model was modified to a 5-zone model in which one-fifth of the fixed carbon gasification occurs in each zone. Thus, both devolatilization and fixed carbon gasification now occur in Zone 0.

Results of the revised model calculations are shown in Table 5-6, zone by zone.*

The measured gas compositions in the bottom of the gasifier indicated that a large fraction of the total carbon gasification had occurred in this zone, as shown by the high concentrations of H_2, CO, CO_2, and CH_4 and the low concentrations of H_2O which were found even in the active central core of the zone. Comparisons of the measured gas compositions and those predicted by the five-zone model are shown below.

Location	Mol %					% of Total Carbon Gasified
	H_2O	CO	CH_4	CO_2	H_2	
Bottom Probe	41.0	8.3	5.8	9.0	33.6	
Top of Zone 1	40.0	8.7	5.2	10.4	32.1	62
Middle Probe	33.1	10.0	7.0	8.3	38.6	
Top of Zone 2	33.7	10.6	6.3	9.4	36.3	74

The probe gas compositions are taken from the plotted data shown in Figures 5-15 and 5-16 and correspond to the probe position at which the H_2O concentration was at the maximum. As shown in Figures 5-15 and 5-16, there are large lateral concentration gradients. The excellent agreement between the probe data and predicted data applies only to the gas compositions near the centerline of the gasifier. In view of the complex gas-solids flow pattern revealed by the probe data, one can only speculate as to the reasons for this agreement.

A general conclusion seems inescapable, however, in that the probe data confirm what the kinetics model predicts - namely, that most of the carbon is gasified within a few feet above the acceptor interface in the gasifier boot.

* The outlet gas composition from Zone 4 does not match exactly that which can be calculated from Table 5-24. To obtain the individual data for each zone, an earlier computerized version of the model had to be used. This version ignores the small amounts of NH_3 and H_2S which are present and does not account for all of the N_2 in the purge gas streams. The maximum difference for any component, except N_2, is 2%.

Basis: 100 lb dry coal fed to gasifier

Zone	0 Atm.	0 Mols	0 Mol Fract.	1 Atm.	1 Mols	1 Mol Fract.	2 Atm.	2 Mols	2 Mol Fract.	3 Atm.	3 Mols	3 Mol Fract.	4 Atm.	4 Mols	4 Mol Fract.
H_2O	5.104	4.1585	.4640	4.399	3.5716	.3999	3.706	2.9986	.3369	3.027	2.4403	.2752	2.376	1.9044	.2160
H_2	3.054	2.4881	.2776	3.533	2.8681	.3212	3.998	3.2343	.3634	4.448	3.5858	.4043	4.858	3.8930	.4416
CO	.770	.6275	.0700	.958	.7774	.0871	1.164	.9414	.1058	1.389	1.1201	.1263	1.634	1.3095	.1486
CH_4	.439	.3571	.0399	.568	.4608	.0516	.697	.5642	.0634	.828	.6676	.0753	.962	.7710	.0875
CO_2	1.239	1.0094	.1126	1.148	.9317	.1043	1.038	.8400	.0944	.910	.7337	.0827	.769	.6165	.0699
N_2	.394	.3208	.0358	.395	.3208	.0359	.396	.3208	.0360	.398	.3208	.0362	.400	.3208	.0364
	11.000	8.9617	.9999	11.001	8.9304	1.0000	10.999	8.8993	.9999	11.000	8.8683	1.0000	10.999	8.8152	1.0000

Carbon	0 Mols	1 Mols	2 Mols	3 Mols	4 Mols
Gas, into zone	.1902(1)	1.9943	2.1699	2.3456	2.5214
$CaCO_3$, into zone	1.1847	.8885	.5924	.2962	0
Gas, out of zone	1.9943	2.1699	2.3456	2.5214	2.6970
$CaCO_3$, out of zone	1.1847	1.1847	.8885	.5924	.2962
Gasified, in zone	1.8041(2)	.4718	.4719	.4720	.4718
Total Gasified	1.8041	2.2759	2.7478	3.2198	3.6916
Carbon Gasified	.49	.62	.74	.87	1
Total Carbon Gasified					
Relative Gasification Rate of Fixed Carbon	1	.55	.35	.20	.084

(1) Carbon in purge gas (recycle and CO_2).
(2) Volatile carbon is 1.3322 atoms.

86

Table 5-6. SUMMARIZED GASIFICATION KINETICS DATA, ZONE BY ZONE, RUN 47B

5.3.4   GAS-SOLIDS CONTACTING AT THE BOTTOM OF THE GASIFIER

Figure 5-14 is a sketch, to scale, of the bottom portion of the gasifier. In the boot, the acceptor is stripped of char so that a clean stream can be fed to the regenerator. At normal process conditions about 70% of the total steam fed to the gasifier enters through the distributor ring at the bottom of the boot. The remainder enters through the distributor ring at the bottom of the transition section leading to the 40-inch diameter gasifier. See Section 11, Book 3, for details of the distributors. The acceptor in the boot is fluidized at a velocity about 10% greater than the incipient fluidization velocity.

During Run 47, Carnegie-Mellon University (under a separate contract with DOE) sampled the gas in the bottom of the gasifier through use of three probes which are shown on the sketch. The tip of each probe could be positioned at any point across the vessel diameter. The probe tip contained a filter to remove solids from the sampled gas stream. The high gas flow rate through the probe prevented any appreciable reactions within the probe. The gas was quenched rapidly to room temperature at system pressure. From the known time of sampling, the weight of condensate, the dry gas meter dial readings, and the dry gas analyses, the gas composition at the tip of the probe was calculated. Details of this work will be published separately.[8]

Figure 5-15 and 5-16 are plots of the data obtained during Run 47B. Since the static pressure at the dry gas meter was not known accurately during some of the sampling periods, the wet gas compositions shown in the figures were calculated from the dry gas compositions assuming that water gas shift equilibrium was attained.

The data show dramatically that poor gas-solids contacting exists at the bottom of the gasifier at all three probe locations. Annular dead zones must exist through which only a small portion of the total steam flows, as shown by the very low steam content and very high CO content which equalled or exceeded the CO content of the product gas leaving the top of the fluidized bed of char.

Figures 5-15 and 5-16 suggest that the bottom of the gasifier is a spouted fluidized bed, as shown schematically in Figure 5-14. The actual flow patterns of gas and solids probably are more complex than would be associated with a simple spout. The flow patterns apparently were stable in Runs 47A and 47B, as indicated by duplicate samples taken several hours apart.

Probe	Distance Across Diameter, inches	Dry Gas Composition, mol %			Sampling Time
		H_2	CO	CH_4	
Middle	40	48.4	22.0	16.6	1708 7 Sept. '77
		46.4	20.8	16.8	0220 8 Sept. '77
Middle	20	57.0	14.3	9.4	1800 7 Sept. '77
		55.7	14.4	9.6	0057 8 Sept. '77
Top	18	55.0	23.0	14.0	0225 30 Sept. '77
		55.8	22.6	14.1	0805 30 Sept. '77

(8) Filo, J. P., Carnegie-Mellon University, Dept. of Chemical Engineering, Ph.D. Thesis. In preparation.
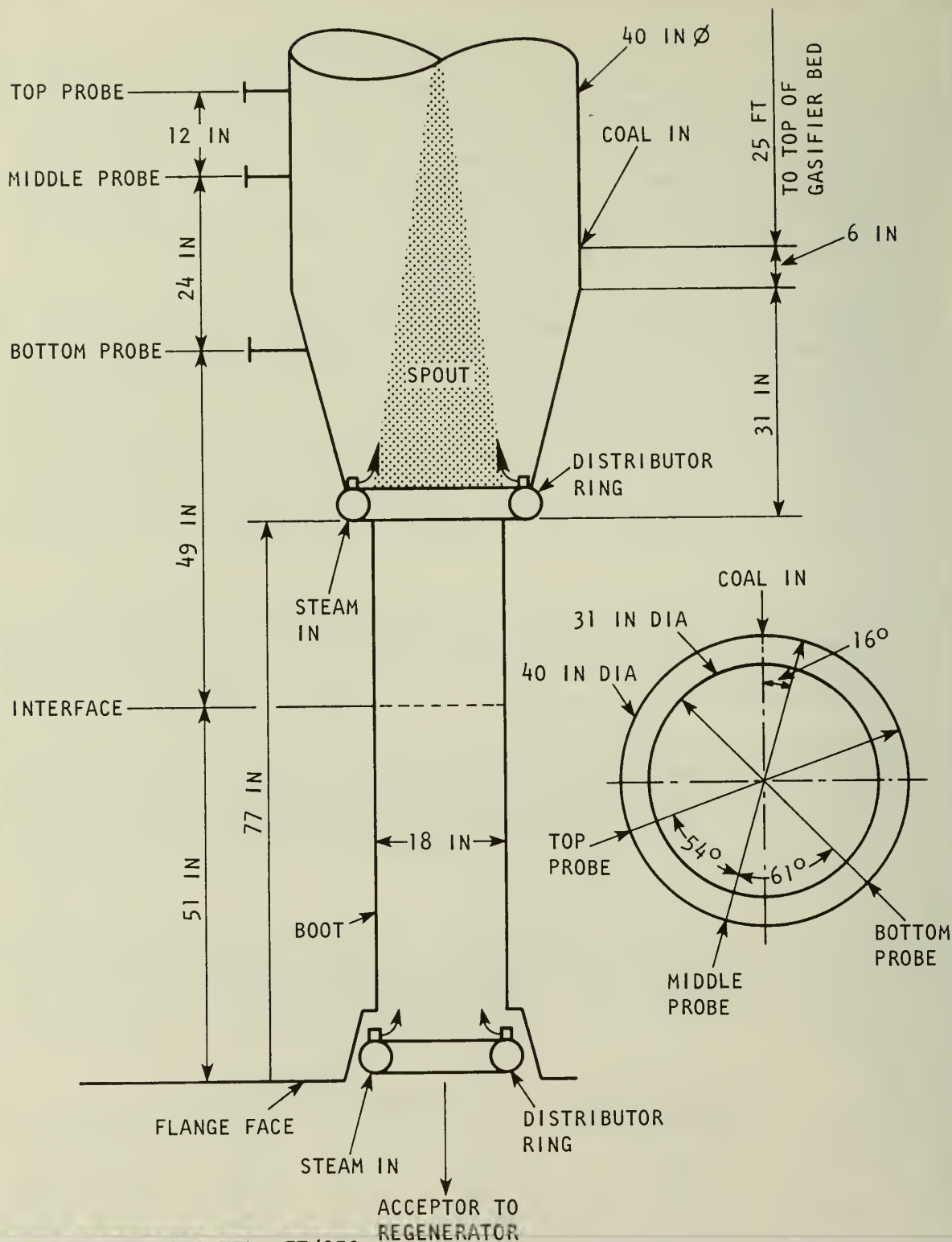
Figure 5-14. SKETCH OF BOTTOM OF GASIFIER SHOWING
PROBE LOCATIONS (DRAWN TO SCALE)
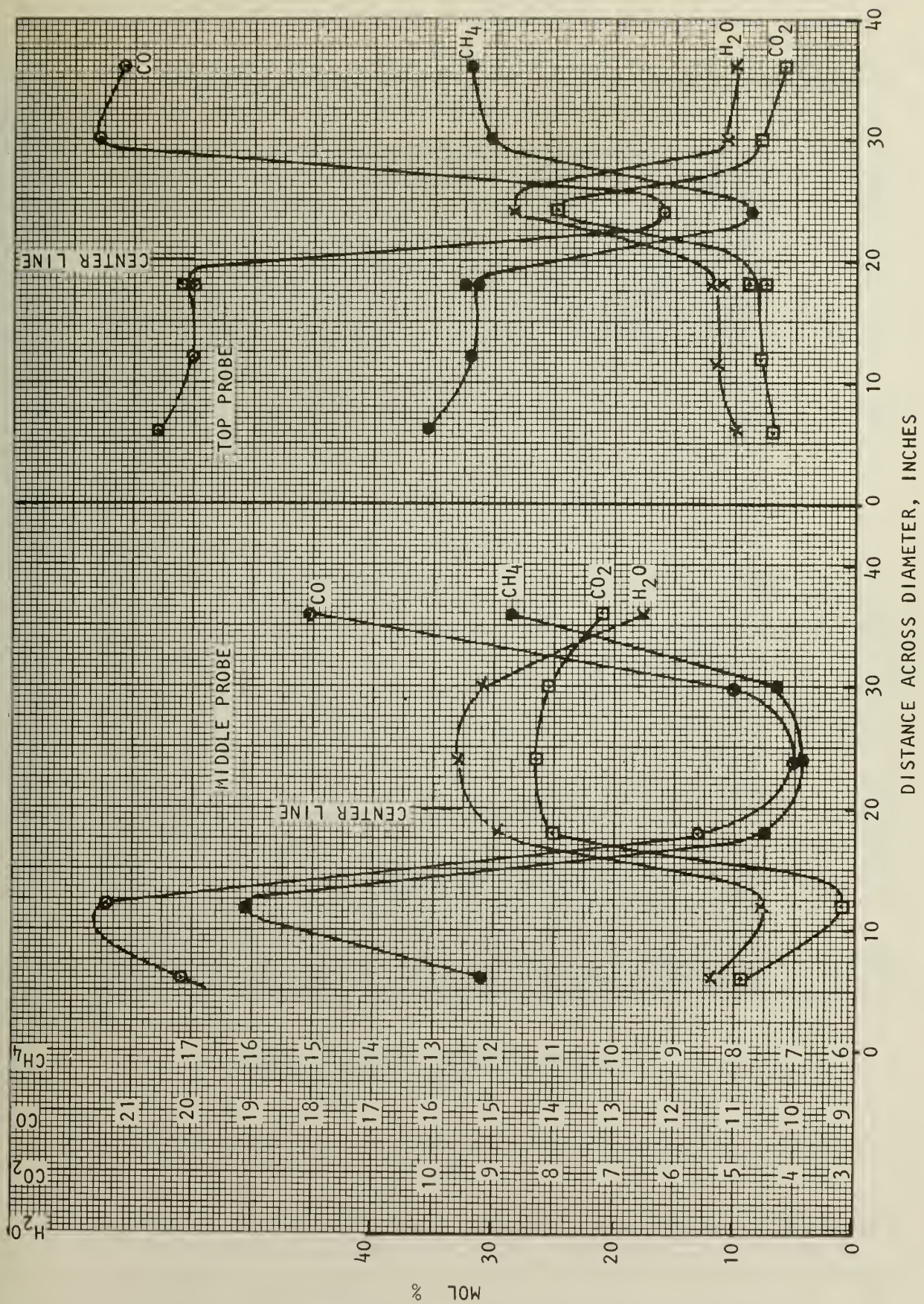
Figure 5-15. GAS COMPOSITION VS. PROBE POSITION, RUN 47B

89
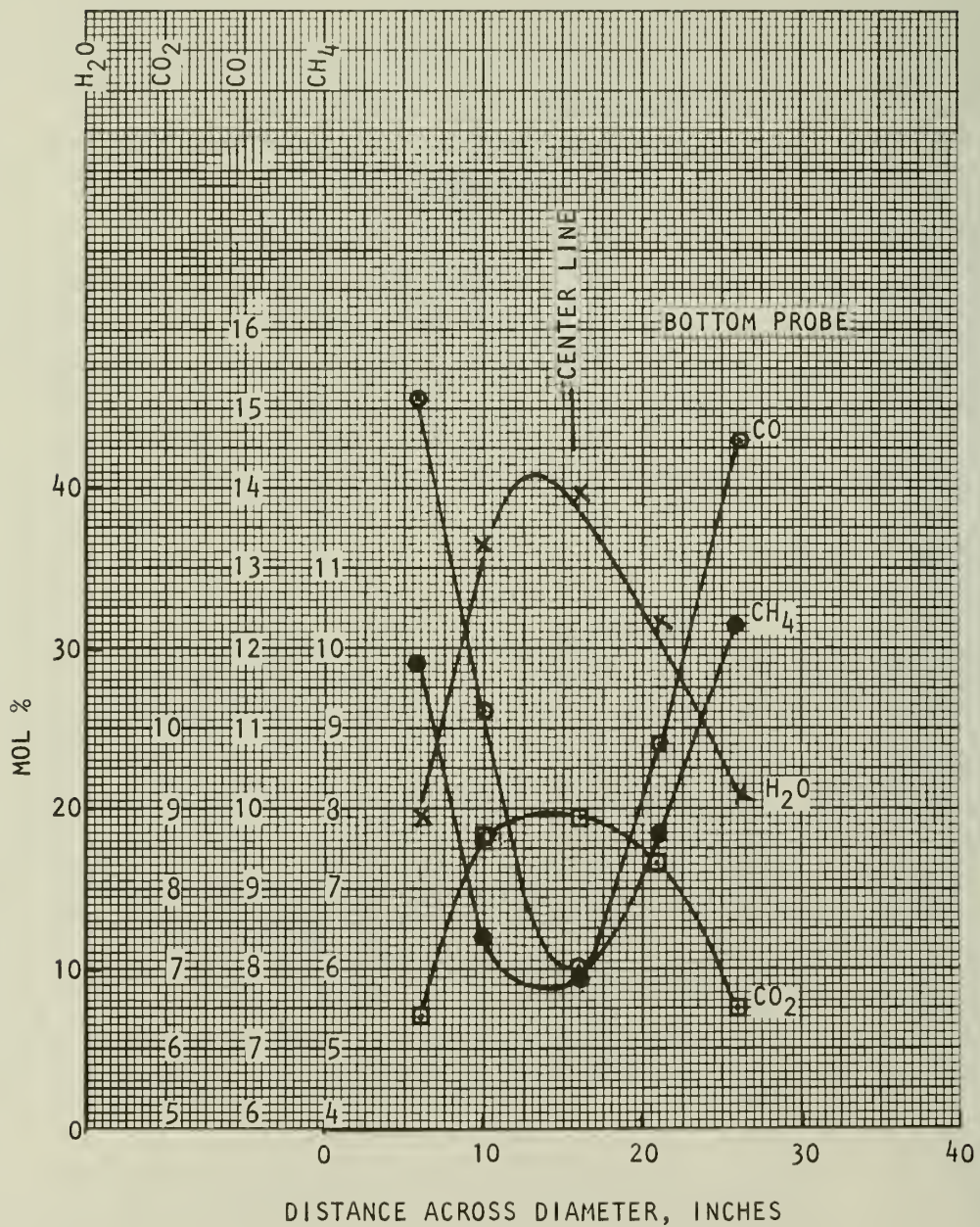
Figure 5-16. GAS COMPOSITION VS. PROBE POSITION, RUN 47B

90

More data taken from probes at different positions around the gasifier periphery and at higher levels in the bed would be needed to better define the flow patterns. Run 47B was the final run in the pilot plant.

The upper distributor ring was installed after Run 7 in 1973 and was used for 4-1/2 years. It is unfortunate that circumstances prevented the taking of samples from the bottom of the gasifier until the final run of the program. Clearly, the ring should have been placed higher in the transition zone, possibly at the top. During plant operations, it was observed repeatedly that the rate at which the showering acceptor could fall into the boot was sensitive to small changes in the flow rate of gas into the boot. The spout-like flow pattern above the boot is consistent with these observations, since the nature of the spout possibly could have been altered drastically by changes in the gas flow rate.

Acquisition of the probe sampling data provided the opportunity to compare the gasification kinetics model with the "real world." The comparison is discussed in 5.3.3.6, above.

5.3.5   GASIFIER BED PROPERTIES AND SHOWERING OF ACCEPTOR

5.3.5.1   Introduction

At process conditions, the acceptor supplies all the gasifier heat duty as it showers downward through the fluidized bed of char. The retention time of the acceptor in the char bed must be sufficient to insure that the recarbonation reaction goes to completion before the acceptor falls into the gasifier boot. From the standpoints of simplicity and reliability, it is desirable to control the retention time without the use of baffles or mechanical devices. The presence of the acceptor in the bed affects the bed density, which in turn affects the pressure balance around the gasifier-regenerator loop.

For process design, it is necessary that the interrelationship of the acceptor circulation rate, acceptor particle properties, and the fluidized bed properties be known. During the pilot plant operations the acceptor was circulated and showered through the gasifier bed for a total of 6400 hours. The data which were obtained provide the base for the process design correlations which are presented here.

In earlier work[1] involving measurement of the retention times of single particles falling through various fluidized beds, the retention times (expressed as the falling velocity) were represented by a power function having the form:

$$V = k_1 \left[\frac{(\rho_s - \rho_B)^{k_2} \phi^{k_3}}{\rho_B^{k_4}} \right] \qquad (5\text{-}42)$$

(1) "Phase II Bench-Scale Research on CSG Process-Studies on Mechanics
    of Fluo-Solids Systems, Jan. 1970. Interim Rpt. No. 3, Book 1,
    Research & Development Rpt. No 16, National Technical Information
    Service PB-184718/AS.

91

<u>Nomenclature</u>

V = Steady-state velocity of the falling particle, ft/sec

ρ_S = Particle density, measured in mercury, lb/ft^3

ρ_B = Density of the fluidized bed, lb/ft^3

ϕ = Diameter of the falling particle, inches

Additional measurements also were made in a continuous system in which acceptor circulated at known rates and was showered through fluidized beds of char at ambient conditions. In order to use Equation 5-42 to predict the mean velocity of a falling cloud of acceptor, the bed density term must account for the presence of the falling acceptor in the bed. The bed density, therefore, is equal to the sum of the density of char in the bed and the density of acceptor in the bed.

$$\rho_B = \rho_{char} + \rho_{acceptor} \tag{5-43}$$

The acceptor density is defined by

$$\rho_{acceptor} = G/V \tag{5-44}$$

where G = the acceptor circulation rate, lb/sec/ft^2 of bed cross-section.

Substitution of Equation 5-43 and 5-44 into Equation 5-42 gives

$$V = k_1 \frac{\left[\rho_S - (\rho_{char} + G/V)\right]^{k_2} \phi^{k_3}}{(\rho_{char} + G/V)^{k_4}} \tag{5-45}$$

The mean falling velocities in the bench-scale continuous system were predicted very well from the correlation based on the single particle data. Because of equipment limitations, the maximum mass flow rate of the showering acceptor was less than one-tenth of the maximum rate achieved in the pilot plant. A new correlation was needed because the pilot plant operated at conditions of lower ρ_S, larger ϕ, and greater G than were used previously.

The early work showed that the falling velocity is independent of the diameter and density of the particles which comprise the fluidized bed. Equation 5-42 predicts that a falling particle will have a finite positive (downward) falling velocity as long as ρ_S is greater than ρ_B, and that the falling velocity is independent of the fluidizing gas velocity. However, as the falling particle size becomes smaller, a limiting condition occurs because the incipient fluidizing velocity of the falling particle approaches the velocity of the gas used to fluidize the bed through which the particle falls. In this situation, the falling particle becomes a bed particle.

In the pilot plant the fluidized bed did not consist entirely of char. Nonchar particles, termed intermediate fines or "junk," in the size range of 20 x 65 mesh, and composed of quartz particles present in the coal ash, built up to an equilibrium concentration in the gasifier bed. The situation described above did occur. The density of the junk particles typically was 110 lb/ft^3, while ρ_B typically was 35 lb/ft^3. A further discussion of the junk particles is given in 5.7.2.3 herein.

To allow for the presence of junk in the fluidized bed, the term, ρ_{char}, in Equation 5-45 was redefined as:

density of nonacceptor in the bed = ρ_{NA}.

The working equation which related the bed and acceptor properties now becomes:

$$ V = k_1 \frac{\left[\rho_s - (\rho_{NA} + G/V)\right]^{k_2} \phi^{k_3}}{(\rho_{NA} + G/V)^{k_4}} \qquad (5\text{-}46) $$

5.3.5.2   Calculation of Needed Quantities from Pilot Plant Operating Data

Nomenclature

I   =   Gasifier bed total inventory, lb. Obtained by pressure drop across the bed and known cross-sectional area (8.72 ft^2).

F   =   Weight fraction acceptor in bed. Obtained by workup of samples taken from the bed near the level of the char outlet line as described in 5.7.1.3, herein. Results of the sample workups are given in Tables 13-29 through 13-39 (Appendices Subsection 13.4 of Book 4).

L   =   Gasifier bed height, ft. above bottom of straight side. Obtained from gasifier pressure tap readings.

M   =   Acceptor circulation rate, leaving the gasifier, lb/hr. Obtained by use of process model described in Subsection 5.3.1, results of which are shown in Tables 5-13 through 5-24.

The derived quantities needed for the correlation are obtained as follows:

V   =   Mean showering velocity, ft/sec = (L)(M)/3600/I/F

ρ_A =   Showering acceptor density, lb/ft^3 = M/3600/8.72/V

ρ_B =   Total bed density, lb/ft^3 = ρ_A/F

ρ_{NA} =   Nonacceptor density, lb/ft^3 = ρ_B - ρ_A

ϕ =   Mean retention time of acceptor, minutes = L/60/V

Numerical values for all of the above are shown in Table 5-7, which follows.

5.3.5.3 Correlation

Use of Equation 5-46 requires the acceptor properties as follows:

ρ_s = Acceptor particle density (measured in mercury), lb/ft^3. Obtained from Tables 13-19 through 13-28, Appendices Subsection 13.4, Book 4 for the specific time of the balance periods shown in Tables 5-13 through 5-24 herein.

ϕ = Acceptor particle diameter, inches. Calculated from Tables 13-19 through 13-28, Appendices Subsection 13.4, Book 4, for the specific time of the balance periods. The arithmetic mean diameter is used.

G = Acceptor circulation rate, $lb/sec/ft^2$ = M/8.72/3600.

Table 5-8 shows all the input data needed for use of Equation 5-46 as well as the predicted values for the mean showering velocity given by the model equation:

$$V = .285 \left[\frac{\phi \left[\rho_s - (\rho_{NA} + \overline{G/V}) \right]}{(\rho_{NA} + G/V)} \right]^{(4/3)} \tag{5-47}$$

Calculation of the individual exponents, as shown in Equation 5-46, gave a correlating equation which produced no appreciable decrease in the mean % difference between the predicted and measured values of V.

5.3.5.4 Relationship of Nonacceptor Bed Density and Junk Content of Gasifier Inventory

The junk or intermediate fines content of the gasifier inventory is given in Tables 13-29 through 13-38, Appendices Subsection 13.4, Book 4. Using the nonacceptor bed densities from Table 5-7, herein, the following simple relationship was derived:

$$\rho_{NA} = 16.7 + .354 \text{ (Wt \% junk)} \tag{5-48}$$

The data used, and the predicted and measured values of ρ_{NA} are shown in Table 5-9. Several other more elaborate relationships involving the char content of the inventory, the measured particle densities, and reciprocal bed densities were investigated. None gave as small a mean % difference between the predicted and measured values of ρ_{NA} as does Equation 5-48.

5.3.6 HEAT AND MATERIAL BALANCES

Tables 5-13 through 5-24 present pilot plant data in the form of heat and material balances. Twelve steady periods were chosen to illustrate the range of conditions which were studied.

Nomenclature	Plant Data				Showering Acceptor Density, lb/ft³ ρ_A	Non-Acceptor Density, lb/ft³ ρ_{NA}	Derived Quantities Total Bed Density lb/ft³ ρ_B	Mean Showering Velocity, ft/sec V	Mean Acceptor Retention Time, min θ
	Bed Inventory, lb I	Wt. Fraction Acceptor in Bed F	Bed Height, ft L	Acceptor Circulation Rate, lb/hr M					
Run									
21-I	8390	.326	24.0	12150	13.071	27.024	40.095	.02961	13.5
21-II	8960	.326	23.4	11800	14.314	29.594	43.908	.02626	14.9
21-III	8980	.372	24.0	11130	15.963	26.948	42.911	.02221	18.0
28B	7000	.412	25.2	14570	13.126	18.733	31.859	.03536	11.9
33B	7300	.403	24.2	15040	13.939	20.649	34.588	.03437	11.7
38C	8060	.464	24.2	12990	17.722	20.472	38.194	.02335	17.3
39	8870	.428	26.1	11750	16.687	22.301	38.988	.02243	19.4
40B	9800	.361	25.2	7664	16.104	28.505	44.609	.01516	77.7
43	8620	.479	28.2	20700	16.792	18.264	35.056	.03927	12.0
46C	6590	.306	28.0	18300	8.259	18.731	26.990	.07058	6.6
47B	7200	.453	26.8	23420	13.968	16.866	30.834	.06341	8.4

Table 5-7. GASIFIER BED DATA USED FOR ACCEPTOR SHOWERING CORRELATION

$$v = .285 \left[\frac{\phi \left[\rho_s - \left(\rho_{NA} + \frac{G}{v} \right) \right]}{\left(\rho_{NA} + \frac{G}{v} \right)} \right]^{(4/3)}$$

(5-47)

Nomenclature Run	Acceptor Particle Density, lb/ft³ ρ_s	Acceptor Particle Diameter, inches ϕ	Non-Acceptor Density, lb/ft³ ρ_{NA}	Acceptor Circulation Rate Lb/hr --	Acceptor Circulation Rate Lb/sec/ft² G	Obs. Mean Showering Velocity, ft/sec V	Calc. Mean Showering Velocity, ft/sec V	% Diff.
21-I	141	.0687	27.024	12150	.38704	.02961	.02745	-7.3
21-II	146	.0687	29.594	11800	.37589	.02626	.02470	-5.9
21-III	144	.0668	26.948	11130	.35455	.02221	.02421	9.0
28B	126	.0749	18.733	14570	.46413	.03536	.03815	7.9
33B	122	.0823	20.649	15040	.47910	.03437	.03512	2.2
38C	113	.0810	20.472	12990	.41380	.02335	.02448	4.8
39	113	.0788	22.301	11750	.37430	.02243	.02263	.9
40B	111	.0745	28.505	7664	.24414	.01516	.01518	.0
45	143	.0689	18.264	20700	.65940	.03927	.03606	-8.2
46C	145	.0808	18.731	18300	.58295	.07058	.07118	.9
47B	138	.0818	16.866	23420	.74605	.05341	.05328	.2
							Mean	4.3
							Standard Deviation	3.4

Table 5-8. CORRELATION OF ACCEPTOR SHOWERING VELOCITY

$$\rho_{NA} = 16.7 + .354 \text{ (wt \% junk)} \qquad (5\text{-}48)$$

Run	% Junk	ρ_{NA} Obs.	ρ_{NA} Calc.	% Diff.
21-I	26.2	27.0	26.0	-3.7
21-II	28.7	29.6	26.8	-9.5
21-III	38.2	26.9	30.2	12.3
28B	7.2	18.7	19.2	2.7
33B	9.8	20.6	20.2	-1.9
38C	9.2	20.5	20.0	-2.4
39	14.2	22.3	21.7	-2.7
40B	27.8	28.5	26.5	-7.0
45	14.1	18.3	21.7	18.6
46C	1.5	18.7	17.2	-8.0
47B	5.4	16.8	18.6	10.7
			Mean	7.2
			Standard Deviation	5.0

Table 5-9. RELATIONSHIP OF NONACCEPTOR BED DENSITY AND
JUNK CONTENT OF BED INVENTORY

5.3.6.1   Notes on Individual Balances

   (1)   Single-Vessel Operation - In two runs the gasifier was isolated
         from the regenerator and the heat duty was supplied by partial
         combustion with air. Balances for these runs are shown in Tables
         5-10 through 5-12.

   (2)   Use of Various Coals

         (a) High-sodium lignite (N. Dakota), Table 5-20.
         (b) Texas lignite, Table 5-21.
         (c) Subbituminous coals.
              1   Sarpy Creek (Montana), Table 5-11.
              2   Wyodak (Wyoming), Tables 5-12, 5-19, and 5-22.
         (d) Otherwise, Velva lignite (N. Dakota) was used.

   (3)   Use of Limestone and Dolomite as Makeup Acceptor

         An Ohio dolomite was used in Runs 21, 26B, and 45. Otherwise, a
         limestone quarried in Rapid City was used. Pilot plant operations
         confirmed the earlier small scale studies which showed that either
         material is suitable as a CO_2 acceptor.

   (4)   Use of Reconstituted Acceptor

         In Run 47, Table 5-24, the acceptor had been reconstituted from
         spent acceptor produced in previous pilot plant runs, as described
         in Book 3, Section 6.

5.3.6.2   Notes on Process Conditions

   (1)   Use of Air in the Gasifier

         The nonprocess use of air was necessary in three runs in order to
         maintain the desired gasifier bed temperature.

         (a) Run 21-III, Table 5-15, and Run 40, Table 5-21: In these runs,
              the accumulation of intermediate fines ("junk") increased
              the gasifier bed density to the extent that sufficient acceptor
              would not shower down through the bed. The "missing" heat
              source was supplied by the addition of air. The existence of
              the junk particles is itself a nonprocess condition, as is
              discussed in 5.7.2.3.
         (b) Run 38C, Table 5-19: In this run, the acceptor particle density
              was low and the acceptor did not shower down through the bed at
              a sufficient rate. Again, the "missing" heat source was supplied
              by air.

         Whenever air was used, a stoichiometric excess of recycle gas was
         fed to the gasifier boot to prevent direct oxidation of the char.

98

Basis: 1 hour
Datum: 60°F, liquid water

	SCF	Lbs	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Coal Feed(1)		1,120	370	103,000	12,790,400
Boot Gas			1530		
Recycle(4)	17,200	1,030		532,900	
Ring Gas			1300		
Air(5)	21,700	1,651		530,600	
Steam	15,350	730		1,212,300	
Purge Gas			60		
Recycle(4)	3,500	209			
Inert(6)	175	14			
Subtotal		4,754		2,378,800	12,790,400
Heats of Reaction					
$CaO + CO_2 = CaCO_3$ .44 Mols at 76,200 Btu/Mol				33,800	
Heat of Combustion In - Heat of Combustion Out				709,400	
Total		4,754		3,122,000	
Output					
Vent Gas(4)	47,400	2,835	1525	1,461,600	9,305,800
Recycle Gas(4)	20,700	1,239	1525	639,000	
Steam	7,870	374	1525	667,800	
H_2S	25.4	2	1525	1,000	16,200
Quench Tower Solids(2)		166	1525	79,500	1,385,500
Purged Char(3)		138	1525	69,800	1,373,500
Subtotal		4,754		2,918,700	12,081,000
Heats of Reaction					
$CaO + S = CaS + O$ .157 Mols at 196,540 Btu/Mol				30,800	
Heat Loss				172,500	
Total		4,754		3,122,000	

	COAL OR CHAR					GAS	
	(1)	(2)	(3)		(4)	(5)	(6)
H, Wt %, Dry	3.91	.40	.53	CH_4, Mol %	3.75		
C	68.10	56.43	66.87	H_2	25.08		
N	.84	.28	.37	CO	24.00		
O	18.14			CO_2	10.35		12.00
S	.64			N_2	36.77	79.00	88.00
Ash				O_2		21.00	
Oxides	8.37	18.10	21.65				
$CaCO_3$		19.61	8.62				
CaS		5.18	1.96				

Table 5-10.   HEAT AND MATERIAL BALANCE - RUN 15B
0900 - 1400 HOURS, DEC. 30, 1973
GASIFIER SYSTEM
PREOXIDIZED VELVA LIGNITE
SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

	SCF	Lbs	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Coal Feed(1)		1,530	375	143,800	17,980,400
Boot Gas					
Recycle(5)	8,730	513	1415	255,800	
Steam	6,500	309	1415	532,800	
Ring Gas					
Air(6)	28,500	2,169	1503	829,700	
Steam	26,500	1,260	1503	2,242,300	
Purge Gas					
Recycle(5)	2,200	129	60		
Inert(7)	200	16	60		
Subtotal		5,926		4,004,400	17,980,400
Heats of Reaction					
$CaO + CO_2 = CaCO_3$ .33 Mols at 76,200 Btu/Mol				25,200	
Heat of Combustion In - Heat of Combustion Out				315,400	
Total		5,926		4,345,000	
Output					
Vent Gas(5)	68,300	4,020	1470	2,094,400	14,023,400
Steam	18,400	875	1470	1,536,200	
Recycle Gas(5)	10,900	642	1470	334,700	
H_2S	89.8	8	1470	3,200	57,400
Quench Tower Solids(2)		52	1470	24,900	497,400
Cyclone Solids(3)		185	1470	92,100	1,932,100
Purged Char(4)		144	1470	66,000	1,154,700
Subtotal		5,926		4,151,500	17,665,000
Heats of Reaction					
$CaO + S = CaS + O$ .12 Mols at 196,540 Btu/Mol				23,600	
Heat Loss				169,900	
Total		5,926		4,345,000	

		COAL OR CHAR					GAS		
	(1)	(2)	(3)	(4)			(5)	(6)	(7)
H, Wt %, Dry	4.55	.62	.85	.52	CH_4, Mol %		5.56		
C	69.49	63.90	69.03	53.45	H_2		28.55		
N	.91	.40	.40	.25	CO		17.55		
O	16.27				CO_2		14.87		12.00
S	.75				N_2		33.47	79.00	88.00
Ash					O_2			21.00	
Oxides	8.03	19.84	19.85	35.05					
$CaCO_3$		12.12	8.40	7.69					
CaS		3.12	1.47	3.04					

Table 5-11.   HEAT AND MATERIAL BALANCE - RUN 31-II
               0000 HOURS TO 2400 HOURS, DEC. 22, 1975
               GASIFIER SYSTEM
               WESTMORELAND SARPY CREEK SUBBITUMINOUS COAL
               SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

	SCF	Lbs	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Coal Feed(1)		1,470	375	138,200	17,297,300
Boot Gas					
Recycle(5)	9,400	556	1411	273,900	
Steam	6,500	309	1411	532,100	
Ring Gas					
Air(6)	29,300	2,231	1515	853,000	
Steam	26,400	1,255	1515	2,236,400	
Purge Gas					
Recycle(5)	2,200	130	60		
Inert(7)	200	16	60		
Subtotal		5,967		4,033,600	17,297,300
Heats of Reaction					
CaO + CO_2 = $CaCO_3$ .251 Mols at 76,200 Btu/Mol				19,100	
Heat of Combustion In - Heat of Combustion Out				380,000	
Total		5,967		4,432,700	
Output					
Vent Gas(5)	68,000	4,014	1480	2,095,500	13,553,500
Steam	19,500	926	1480	1,630,100	
Recycle Gas(5)	11,600	686	1480	357,100	
H_2S	93.6	8	1480	3,400	59,800
Quench Tower Solids(2)		44	1480	21,100	410,300
Cyclone Solids(3)		153	1480	77,300	1,617,100
Purged Char(4)		136	1480	65,100	1,276,600
Subtotal		5,967		4,249,600	16,917,300
Heats of Reaction					
CaO + S = CaS + O .065 Mols at 196,540 Btu/Mol				12,700	
Heat Loss				170,400	
Total		5,967		4,432,700	

		COAL OR CHAR					GAS	
	(1)	(2)	(3)	(4)		(5)	(6)	(7)
H, Wt %, Dry	4.88	.59	.88	.58	CH_4, Mol %	5.21		
C	69.35	62.38	69.80	62.98	H_2	28.42		
N	.95	.38	.44	.29	CO	16.93		
O	17.52				CO_2	14.88		12.00
S	.68				N_2	34.56	79.00	88.00
Ash					O_2		21.00	
Oxides	6.62	24.88	18.85	29.34				
$CaCO_3$		9.16	9.04	5.32				
CaS		2.61	.99	1.49				

Table 5-12.   HEAT AND MATERIAL BALANCE - RUN 31-III
0600 HOURS DEC. 27 TO 0800 HOURS DEC. 28, 1975
GASIFIER SYSTEM
WYODAK SUBBITUMINOUS COAL
SYSTEM PRESSURE 150 PSIG

(2) Use of Recycle Gas

The nonprocess use of recycle gas, other than that just described, was necessary for the following reasons:

(a) In early runs prior to Run 28B, Table 5-17, recycle gas was fed to the gasifier boot to decrease the partial pressure of steam. This expedient was adopted to insure that there was no possibility of formation, during process upsets, of sticky liquids in the system, $CaO-Ca(OH)_2 - CaCO_3$. The emphasis during this period was on improving plant reliability.

(b) Run 39, Table 5-20: In previous runs with the high-sodium Glenharold lignite, it was found that sticky liquids formed at the normal boot steam partial pressure of 11.6 atm. Laboratory work described in Section 5.7 showed that the liquids did not form at steam partial pressures of less than 10 atm. Rather than to decrease the plant system pressure, it was expedient to dilute the steam with recycle gas.

(c) Run 46C, Table 5-23: This was the only run in which the plant system pressure was anything other than 150 psig (11.1 atm abs). The pressure was increased to 190 psig (13.9 atm abs) and the steam was diluted with recycle gas. The purpose of the run was to determine the maximum steam partial pressure at which no sticky liquids formed. During the run, the steam partial pressure was increased in a stepwise manner by decreasing the ratio of recycle gas to steam.

(3) Use of Regenerator Auxiliary Fuel

Beginning with Run 26, auxiliary fuel was fed to the regenerator, as described in Subsection 5.4.3. The intent was to compensate for the nonprocess char loss through the gasifier cyclone. In Run 45, Table 5-22, the heating value of the auxiliary fuel was more than twice that of the cyclone solids. The higher rate was used to allow a decrease in coal feed rate in order to achieve a higher level of fixed carbon conversion.

5.3.6.3   Summarized Run Conditions and Results

For ready comparisons among the twelve steady periods, salient run conditions from Tables 5-13 through 5-24 are summarized in Table 5-25. Also shown are run results which are not stated explicitly in these tables. Similarly, the heat balances are summarized in Table 5-26.

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Coal Feed(1)	2,550		400	263,800	27,800,000
Acceptor(8)	10,826		1850	4,726,400	
Boot Gas			1465		
Recycle(9)	1,002	12,030		375,300	
Steam	56	21,070		1,754,800	
CO₂		480		20,400	
Ring Gas			1465		
Steam	1,806	38,000	60	3,164,800	
Purge Gas					
Recycle(9)	81	5,950			
Inert(11)	56.5	1,030			
H₂		760			
Subtotal	16,377.5			10,305,500	27,800,000
Heat of Reaction CaO + CO₂ = CaCO₃ 30,856 Mols at 76,200 Btu/Mol				2,351,200	
Total	16,377.5			12,656,700	

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char					
To Regenerator(2)	736	56,460	1480	370,500	7,868,900
Cyclone Loss(3)	114	17,980	1480	55,700	1,097,600
Acceptor(7)		29,320	1480	4,210,900	
To Regenerator	11,860				
Reject	292			103,700	
Gas			1480		
Product(9)	1,954	56,460		1,783,200	21,439,100
Recycle(9)	1,394	17,980		567,800	
Steam		29,320		2,453,200	
H₂S	8.5	55		3,400	60,600
NH₃	19	420		17,700	181,800
Subtotal	16,377.5			9,566,100	30,648,000
Heat of Combustion (Output – Input ex-Acceptor)					
CaO + S = CaS + O 0.227 Mols at 196,540 Btu/Mol				2,848,000	
				44,600	
Heat Loss				198,000	
Total	16,377.5			12,656,700	

REGENERATOR

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(2)	736		1480	370,500	7,868,900
Acceptor					
From Gasifier(7)	11,860		1480	4,210,900	
Make-up(6)	560		60		
Ring Gas			830		
Air(12)	5,706	74,960		1,098,400	
Moisture	21	440		29,400	
Acceptor Lift Gas			1230		
Recycle(10)		50,470		1,296,200	
Moisture	14	290		22,700	
Char Lift Gas			750		
Inert(11)	553	7,000		92,600	
Recycle(10)		430		6,200	
Moisture	.1	3		200	
Purge			60		
Recycle(10)	72	1,200			
Inert(11)		910			
H₂	6.3	85			
Subtotal	19,528.4			7,127,100	7,868,900
Heat of Reaction				7,074,400	
Heat of Combustion (Input – Output ex-Acceptor) CaS + O = CaO + S 0.159 Mols at 196,540 Btu/Mol				11,600	
Total	19,528.4			14,213,100	

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(4)	186		1850	86,000	149,400
Acceptor(8)	10,826		1850	4,726,400	
To Gasifier	46			20,000	
Overhead					
Gas			1850		
Flue(10)	8,386	97,070		4,024,500	637,400
Recycle(10)		52,100		2,160,300	
Steam	81	1,700		159,200	
COS	1.2	7.3		400	4,600
H₂S	0.4	5		200	3,100
SO₂	1.7	10		600	
Subtotal	19,528.3			11,177,600	794,500
Heat of Reaction MgCO₃ = MgO + CO₂ 3.115 Mols at 45,000 Btu/Mol CaCO₃ = CaO + CO₂ 32,681 Mols at 76,200 Btu/Mol				140,200 2,490,300	
Heat Loss				405,000	
Total	19,528.3			14,213,100	

LIGNITE OR CHAR

H, Wt %, Dry	(1)	(2)	(3)	(4)
C	4.32	.73	.70	5.64
H	65.15	71.26	64.12	
N	1.01	.41	0.40	
O	20.78			
S	.60			
Ash	H.14			
Oxides	18.35	.06	23.56	89.02
CaS	.06		1.60	5.34
CaCO₃	9.13		9.62	

	(5)	(6)
CaO, Wt %		
CaCO₃	47.47	
MgO	46.91	
MgCO₃		
CaS	5.62	
Inert		

ACCEPTOR

(7)	(8)	
29.39	48.68	
24.77	41.04	
36.56		
.116		
9.16	10.28	

GAS

	(9)	(10)	(11)	(12)
CH₄, Mol %	14.50	.04		
H₂	57.05	2.00		
CO	14.87	29.65	12.00	
CO₂	10.46	68.31	88.00	79.00
N₂	3.12			21.00
O₂				

Table 5-13. HEAT AND MATERIAL BALANCE - RUN 21 (BALANCE I)
1900 HOURS SEPTEMBER 9 TO 0300 HOURS SEPTEMBER 10, 1974
VELVA LIGNITE SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Coal Feed(1)	2,600		400	269,000	28,305,400
Acceptor(8)	10,433		1860	4,582,800	
Boot Gas			1465		
Recycle(9) Steam	988	12,800		398,700	
CO₂	56	20,780		1,730,200	
		480		20,400	
Ring Gas Steam	1,854	39,000	1465	3,248,100	
Moisture					
Purge Recycle(9)	81	6,000	60		
Inert(11)	56.5	1,030			
N₂		760			
Subtotal	16,068.5			10,249,200	28,305,400
Heats of Reaction CaO + CO₂ = CaCO₃ 32.017 Mols at 76,200 Btu/Mol				2,439,700	
Total	16,068.5			12,688,900	
Output					
Cbar					
To Regenerator(2)	768		1480	390,400	8,386,700
Cyclone Losses(3)	106		1530	53,700	1,024,100
Acceptor(?) To Regenerator			1560		
Reject					
Gas					
Product(9)	1,915	56,000(56,249)*	1480	1,834,300	21,396,500
Recycle(9)		18,800(18,887)		616,000	
Steam	1,450	30,500(30,161)		2,592,600	
H₂S	8.6	96		3,600	
NH₃	18	400		17,700	61,300
					174,400
Subtotal	16,068.6			9,710,700	31,043,000
Heats of Reaction Heat of Combustion (Output - Input ex-Acceptor)					
CaO + S = CaS + O 0.217 Mols at 196,540 Btu/Mol				2,737,600	
Heat Loss				198,000	
Total	16,068.6			12,688,900	

REGENERATOR

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char(2)	768		1480	390,400	8,386,700
Acceptor From Gasifier(7)	11,509		1480	4,097,600	
Make-up(6)	560		60		
Ring Gas Steam			830		
Air(12)	5,903	77,550		1,136,300	
Moisture	22	450		30,500	
Acceptor Lift Gas Recycle(10)		49,840	1240	1,289,700	
Moisture	14	290		22,500	
Char Lift Gas Inert(11)	553	7,000	750	92,600	
Recycle(10)		530		7,600	
Moisture	0.1	3		200	
Purge Gas Recycle(10)		1,210			
Inert(11)		910			
N₂	72	85	60		
	6.3				
Subtotal	19,407.4			7,067,400	8,386,700
Heats of Reaction Heat of Combustion (Input - Output ex-Acceptor)				7,227,900	
CaS + O = CaO + S 0.058 Mols at 196,540 Btu/Mol				11,400	
Total	19,407.4			14,306,700	
Output					
Char(4)	176		1860	82,200	159,100
Acceptor(8) To Gasifier	10,433		1860	4,582,800	
Overhead	46			20,200	
Gas Flue(10)	8,665	100,620	1860	4,185,600	991,700
Recycle(10)		51,620		2,147,200	
Steam	84	1,770		166,600	
COS	1.2	7.5		500	4,700
H₂S	0.5	5.2		200	3,300
SO₂	1.6	9.3		600	
Subtotal	19,407.3			11,185,900	1,158,800
Heats of Reaction MgCO₃ = MgO + CO₂ 3.115 Mols at 45,000 Btu/Mol				140,200	
CaCO₃ = CaO + CO₂ 33.801 Mols at 76,200 Btu/Mol				2,575,600	
Heat Loss				405,000	
Total	19,407.3			14,306,700	

LIGNITE OR CHAR

	(1)	(2)	(3)	(4)
H, Wt %, Dry	4.31	.76	.61	6.34
C	65.18	72.70	64.99	
N	.95	.43	.42	
O	21.52			
S	.58			
Ash				
Oxides	7.46	14.89	23.37	88.10
CaS		.052	1.260	5.56
CaCO₃		11.17	9.35	

ACCEPTOR

	(6)	(7)	(8)
CaO, Wt %	47.47	28.18	48.68
CaCO₃	46.91	26.34	41.03
MgO		36.27	
MgCO₃			
CaS		.118	
Inert	5.62	9.09	10.29

GAS

	(9)	(10)	(11)	(12)
CH₄, Mol %	14.60(14.53)*	.07		
H₂	57.28(57.48)	3.00		
CO	15.05(14.54)	29.00	12.00	79.00
CO₂	9.94(10.33)	67.93	88.00	21.00
N₂	3.13(3.12)			
O₂				

NOTE: The gasifier bed temperature was 1480°F. The bed level was somewhat low in this run, such that the surging bed did not cover the stream of hot acceptor entering the gasifier. The result was that the gas leaving the gasifier was heated to 1530°F, as measured by thermocouples above the entering acceptor stream. The numbers in parentheses are the flows and compositions at the top of the bed.

Table 5-14. HEAT AND MATERIAL BALANCE - RUN 21 (BALANCE II)
2300 HOURS SEPTEMBER 11 TO 0500 HOURS
SEPTEMBER 12, 1974 VELVA LIGNITE SYSTEM
PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Coal Feed(1)	2,500		400	258,600	27,245,100
Acceptor(8)	9,981		1850	4,357,500	
Soot Gas			1465		
Recycle(9)	1,024	8,460		255,800	
Steam		21,550		1,794,700	
CO₂	56	480		20,400	
Ring Gas			1465		
Steam	1,499	31,540		2,626,900	
Air(12)	530	6,960		192,200	
Purge			60		
Recycle(9)	81	5,420			
Inert(11)	120	1,030			
N₂		1,620			
Subtotal	15,791				
Heat of Reaction					
CaO + CO₂ = CaCO₃ 26.916 Mols at 76,200 Btu/Mol				2,051,000	
Total	15,791			9,506,100 / 11,557,100	27,245,100

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char					
To Regenerator(2)	704		1500	361,500	7,522,200
Cyclone Loss(3)	111		1500	54,640	1,020,400
Acceptor(7)			1500		
To Regenerator	10,838			3,898,400	
Reject	290			104,300	
Gas					
Product(9)	2,582	64,730	1500	2,011,500	20,704,400
Recycle(9)	1,240	13,880		431,200	
Steam		26,090		2,196,900	
H₂S	8.9	78		2,800	48,800
NH₃	19	410		17,900	180,000
Subtotal	15,780.9			8,079,100	29,475,800
Heat of Combustion (Output - Input ex-Acceptor)					
CaO + S = CaS + O 0.251 Mols at 196,540 Btu/Mol				2,230,700	
Heat Loss				198,000	
Total	15,780.9			11,557,100	29,475,800

REGENERATOR

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(2)	704		1500	361,500	7,522,200
Acceptor					
From Gasifier(7)	10,838		1500	3,898,400	
Make-up(6)	560		60		
Ring Gas					
Air(12)	5,299	69,620	830	1,020,200	
Moisture	19	410		27,300	
Acceptor Lift Gas					
Recycle(10)		49,950	1250	1,300,100	
Moisture	14	290		22,600	
Char Lift Gas					
Inert(11)	553	7,000	750	92,600	
Recycle(10)		620		8,900	
Moisture	0.2	4		200	
Purge					
Recycle(10)		1,210	60		
Inert(11)	72	910			
N₂	13	180			
Subtotal	18,072.2			6,731,800	
Heats of Reaction (Input - Output ex-Acceptor)					
Heat of Combustion 0.066 Mols at 196,540 Btu/Mol				13,000	
CaC + O = CaO + S				6,477,500	7,522,200
Total	18,072.2			13,222,300	

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(4)	170		1850	78,800	143,000
Acceptor(8)	9,981		1850	4,357,400	
To Gasifier					
Overhead	46			20,000	
Gas					
Flue(10)	7,795	90,790	1850	3,742,400	894,600
Recycle(10)		51,780		2,134,600	
Steam	76	1,590		149,100	
COS	1.1			400	4,200
H₂S	0.4	6.7		200	2,900
SO₂	2.4	4.5		800	
Subtotal	18,071.9			10,483,700	
Heats of Reaction					
MgCO₃ = MgO + CO₂ 3.115 Mols at 45,000 Btu/Mol				140,200	
CaCO₃ = CaO + CO₂ 28.785 Mols at 76,200 Btu/Mol				2,193,400	
Heat Loss				405,000	
Total	18,071.9			13,222,300	1,044,700

LIGNITE OR CHAR

H, Wt %, Dry	(1)	(2)	(3)	(4)
H	4.47	0.72	0.71	5.89
C	64.70	71.28	61.16	
N	1.02	0.40	0.42	
O	21.45			
S	0.58			
Ash	7.78	15.86		87.55
Oxides				6.56
CaS		0.05	1.53	
CaCO₃		11.69	9.83	

ACCEPTOR

	(7)	(8)
CaO, Wt %	30.56	48.68
CaCO₃	23.372	
MgO	38.80	41.04
MgCO₃	0.144	
CaS	9.13	
	47.46	
	48.91	
	5.63	10.28

GAS

	(9)	(10)	(11)	(12)
CH₄, Mol %	10.10	0.07		
H₂	51.19	3.00		
CO	16.00			
CO₂	10.17	28.45	12.00	79.00
N₂	12.54	68.48	88.00	21.00

Table 5-15. HEAT AND MATERIAL BALANCE - RUN 21 (BALANCE III)
1900 HOURS TO 2300 HOURS SEPTEMBER 12, 1974
VELVA LIGNITE SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char					
Coal Feed(1)	2,450		400	253,400	27,597,700
Acceptor(8)	9,594		1840	4,157,000	
Boot Gas			1430		
Recycle(9)	1,573	14,600		433,000	
Steam		33,080		2,725,000	
Ring Gas			1505		
Steam	1,046	22,000		1,855,700	
Purge			60		
Recycle(9)	18	3,360			
Inert(11)	93	230			
H₂		1,260			
Subtotal	14,774			9,424,100	27,597,700
Heats of Reaction					
CaO + CO₂ = CaCO₃ 32.676 Moles at 76,200 Btu/Mol				2,489,900	
Total	14,774			11,914,000	

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char					
To Regenerator(2)	625		1495	325,700	6,658,800
Reject(2)	75		1495	39,000	823,000
Cyclone Losses(3)	100		1495	49,500	900,200
Acceptor(7)	10,686			3,861,000	
To Regenerator	256		1495	107,000	
Reject					
Gas					
Product(9)	1,799	57,050		1,782,000	21,656,900
Recycle(9)	1,170	17,960		540,500	
Steam		34,620		2,070,400	
H₂S	5.4	60		2,200	38,100
N₂	18	400		17,100	172,900
Subtotal	14,774.4			8,813,500	30,449,900
Heats of Reaction					
Heat of Combustion (Output – Input ex-Acceptor)					
CaO + S = CaS + O 0.256 Moles at 196,540 Btu/Mol				2,852,200	
Heat Loss				198,000	
Total	14,774.4			11,914,000	

	(1)	(2)	(3)	(4)	(5)
H, Wt %, Dry	4.59	.83	.78		2.20
C	65.16	72.79	59.10	7.19	74.30
O	1.30	.36	.22		.80
N	20.87				7.20
Ash	.54				1.50
Oxides	6.84	10.35	23.26	83.76	14.00
CaS		.319	2.183	9.05	
CaCO₃		15.35	14.46		
Wt %, Moisture					3.95

REGENERATOR

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(2)	625		1455	325,700	6,858,900
Auxiliary Fuel(5)	106		60		1,235,300
Moisture	4	88			
Acceptor			1495		
From Gasifier(7)	10,686			3,861,000	
Make-up(6)	560		60		
Ring Gas			830		
Air(12)	5,806	76,280		1,117,600	
Moisture	21	440		30,000	
Acceptor Lift Gas			1175		
Recycle(10)		49,490		1,205,400	
Moisture	14	290		21,900	
Char Lift Gas			725		
Inert(11)	553	7,000		89,100	
Recycle(10)		2,860		39,600	
Moisture	1	17		1,100	
Purge Gas			60		
Recycle(10)	43	1,930			
Inert(11)	10	540			
N₂		140			
Subtotal	18,425			6,691,400	8,094,100
Heat of Reaction (Input – Output ex-Acceptor)					
CaO + O = CaO + S 0.030 Mole at 196,540 Btu/Mol				5,900	
Total	18,429			13,914,000	

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(4)	149		1840	68,300	152,100
Acceptor(8)			1840		
To Gasifier	9,594			4,157,000	
Overhead	46			19,800	
Gas			1840		
Flue(10)	8,531	98,700		4,069,200	716,900
Recycle(10)		54,280		2,237,600	
Steam	104	2,130		204,400	
COS	1.1	7.2		400	4,500
H₂S	0.6	6.1		300	3,900
SO₂	2.9	17		1,000	
Subtotal	18,428.6			10,758,000	877,400
Heats of Reaction					
MgCO₃ = MgO + CO₂ 3.111 Mole at 45,000 Btu/Mol				140,000	
CaCO₃ = CaO + CO₂ 34.285 Mole at 76,200 Btu/Mol				2,611,000	
Heat Loss				405,000	
Total	18,428.6			13,914,000	

ACCEPTOR	(6)	(7)	(8)
CaO, Wt %		27.25	49.70
CaCO₃	48.20	28.67	41.22
MgO	46.86	36.01	
MgCO₃		.128	
CaS	4.94	7.94	9.08
Inert			

GAS	(9)	(10)	(11)	(12)
CH₄, Mol %	13.20	.06		
H₂	50.73	2.20		
CO	15.20	29.78	12.00	
CO₂	8.14	67.96	88.00	79.00
N₂	2.73			21.00
O₂				

Table 5-16. HEAT AND MATERIAL BALANCE – RUN 26B
0000 TO 0300 HOURS JUNE 16, 1975 VELVA LIGNITE
SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Lignite Feed(1)	2,570		400	265,900	28,912,500
Acceptor(8)	13,258		1840	5,112,700	
Boot Gas			1400		
Steam	1,806			3,099,800	
CO₂	104	34,000		36,300	
Ring Gas		900			
Steam	761	16,000	1500	1,347,500	
Purge Gas			60		
Recycle(9)		3,170			
Inert(11)	20	250			
N₂	103	1,395			
Subtotal	18,622			9,862,200	28,912,500
Heats of Reaction					
CaO + CO₂ = CaCO₃ 30.824 Mols at 76,200 Btu/Mol				2,348,800	
Total	18,622			12,211,000	
Output					
Char					
To Regenerator(2)	537		1490	276,100	8,050,800
Reject(2)	114		1490	58,600	1,283,900
Cyclone Loss(3)	122		1490	60,300	1,246,500
Acceptor(7)					
To Regenerator	14,275		1490	4,594,000	
Reject	296			95,100	
Gas					
Product(9)	2,191	62,150	1490	1,956,900	23,053,200
Recycle(9)		3,170		99,700	
Steam	1,064	22,380		1,878,400	
H₂S	6	70		2,600	44,800
NH₃	17	388		16,600	168,700
Subtotal	18,622			9,038,300	31,847,900
Heats of Reaction (Output - Input ex-Acceptor)				2,935,400	
CaO + S = CaS + O .200 Mols at 196,540 Btu/Mol				39,300	
Heat Loss				198,000	
Total	18,622			12,211,000	

LIGNITE OR CHAR

	(1)	(2)	(3)	(4)	(5)
H, Wt %, Dry	4.42	.65	.45		2.18
C	66.73	75.57	69.20	8.39	74.44
N	.93	.34	.43		.61
O	21.90				9.27
S	.48				1.77
Ash	5.54		12.22	81.39	11.53
CaS		10.08	1.94	10.22	
CaCO₃		13.03	15.76		
Wt %, Moisture					5.29

REGENERATOR

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char(2)	537		1490	276,100	6,050,800
Auxiliary Fuel(5)	192	213	60		2,212,500
Moisture	10				
Acceptor					
From Gasifier(7)	14,275		1490	4,594,000	
Make-up(6)	560		60		
Ring Gas					
Air(12)	5,791	76,100	830	1,114,700	
Moisture	21	444		29,900	
Acceptor Lift Gas					
Recycle(10)		50,540	1400	1,505,500	
Moisture	14	295		24,000	
Char Lift Gas					
Inert(1)	553	7,000	760	94,100	
Recycle(10)		2,890		42,100	
Moisture	1	17		1,100	
Purge					
Recycle(10)		2,000	60		
Inert(11)	8	100			
N₂	12	155			
Subtotal	21,974			7,681,500	8,263,300
Heats of Reaction					
Heat of Combustion (Input - Output ex-Acceptor)				7,126,600	
Total	21,974			14,808,100	
Output					
Char(4)	131		1840	60,400	156,400
Acceptor(8)	13,258		1840	5,112,700	
To Gasifier					
Overhead	48	2,320		18,300	
Gas					
Flue(10)	6,422	97,900	1840	4,018,300	971,800
Recycle(10)		55,430		2,275,800	
Steam	110	2,320		216,700	
COS	1.1	7.0		400	
H₂S	0.6	6.5		300	4,400
SO₂	2.8	16.8		1,000	4,100
Subtotal	21,973.5			11,704,100	1,136,700
Heats of Reaction					
MgCO₃ = MgO + CO₂, 0.151 Mols at 45,000 Btu/Mol				6,800	
CaCO₃ = CaO + CO₂, 35.264 Mols at 75,200 Btu/Mol				2,687,100	
CaS + O = CaO + S, 0.026 Mols at 196,540 Btu/Mol				5,100	
Heat Loss				405,000	
Total	21,974			14,808,100	

ACCEPTOR

	(6)	(7)	(8)
CaO, Wt %	96.24	75.32	95.44
CaCO₃		20.46	1.92
MgO	2.27	1.75	
MgCO₃		0.0678	
CaS	1.49	2.40	2.64
Inert			

GAS

	(9)	(10)	(11)	(12)
CH₄, Mol %	13.00	0.09	12.00	79.00
H₂	56.75	3.00	88.00	21.00
CO	17.15	28.92		
CO₂	10.35	67.99		
N₂	2.75			
O₂				

Table 5-17. HEAT AND MATERIAL BALANCE - RUN 28B
1900 HOURS SEPTEMBER 26 TO 0700 HOURS
SEPTEMBER 27, 1975 VELVA LIGNITE SYSTEM
PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Coal Feed(1)	2,770		400	286,600	30,608,500
Acceptor(8)	13,595		1845	5,258,300	
Boot Gas			1430		
Steam	1,937	40,750		3,356,200	
CO₂	109	940		38,800	
Ring Gas	744	15,650	1500	1,318,000	
Steam					
Purge Gas					
Recycle(9)		3,100			
Inert(11)	16				
N₂	111	1,500			
Subtotal	19,282			10,257,900	30,608,500
Heat of Reaction					
CaO + CO₂ = CaCO₃	33,761 Mols at 76,200 Btu/Mol			2,572,600	
Total	19,282			12,830,500	12,830,500
Output					
Char					
To Regenerator(2)	710		1490	363,500	7,991,300
Cyclone Loss(3)	131		1520	68,000	1,349,800
Acceptor(7)	15,043		1490	4,857,800	
To Regenerator			1520		
Gas					
Product(9)	2,248.5	64,700(64,929)*		2,080,800	24,144,200
Recycle(9)		3,100 (3,044)		98,500	
Steam	1,125	23,673(23,435)		2,006,200	
H₂S	8.5	72		2,700	45,900
NH₃	18	396		17,400	172,100
Subtotal	19,282			9,495,200	33,703,300
Heat of Combustion (Output – Input ex-Acceptor)					
CaO + S = CaS + O	0.216 Mols at 196,540 Btu/Mol				
Heat Loss				3,094,800	
				42,500	
				198,000	
Total	19,282			12,830,500	12,830,500

REGENERATOR

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char(2)	710		1490	363,500	7,991,300
Auxiliary Fuel(5)	65		60		680,000
Moisture	1	19			
Acceptor					
From Gasifier(7)	15,043		1490	4,857,800	
Make-up(6)	560		60		
Ring Gas			840		
Air(12)	8,196	81,400		1,208,900	
Moisture	23	475		32,000	
Acceptor Lift Gas					
Recycle(10)	15	54,800	1360	1,583,700	
Steam		320		25,800	
Char Lift Gas					
Inert(11)	553	7,000	770	95,600	
Recycle(10)		2,960		44,000	
Moisture	0.8	17		1,100	
Purge Gas					
Recycle(10)		2,200	60		
Inert(11)		1,000			
N₂	12.2	170			
Subtotal	23,258			8,212,400	8,671,300
Heat of Reaction					
CaS + O = CaO + S	0.028 Mols at 196,540 Btu/Mol			5,500	
Total	23,258			15,850,800	
Output					
Char(4)	181		1845	74,500	165,400
Acceptor(8)			1845		
To Gasifier	13,595			5,258,300	
Overhead	48			18,400	
Reject(2)	269			104,000	
Gas					
Flue(10)	9,092	105,331	1845	4,350,700	864,700
Recycle(10)		59,960		2,478,200	
Steam		1,877		175,800	
COS	1.2	8		500	4,900
H₂S	0.5	5		200	3,400
SO₂	2.3	14		800	
Subtotal	23,258			12,461,400	1,038,400
Heat of Reaction					
MgCO₃ = MgO + CO₂	0.151 Mols at 45,000 Btu/Mol			6,800	
CaCO₃ = CaO + CO₂	38,953 Mols at 76,200 Btu/Mol			2,968,200	
Heat Loss				414,400	
Total	23,258			15,850,800	

Composition Analyses

Coal or Char / Gasifier

	COAL OR CHAR			GASIFIER	
H, Wt %, Dry	(1)	(2)	(3)	(4)	(5)
H	4.40	.65	.72	0.00	1.97
C	65.83	75.51	68.68	7.21	67.58
N	.88	.37	.35		.74
O	22.45				8.91
S	.47				2.12
Ash	5.97				18.68
Oxides		12.97	14.39	85.32	
CaS		.43	1.17	7.47	
CaCO₃		10.07	14.69		
Wt %, Moisture					1.39

	(6)
	96.24
	2.27
	1.49

ACCEPTOR

	(7)	(8)
CaO, Wt %	73.95	95.44
CaCO₃	21.86	1.92
MgO	1.74	
MgCO₃	.073	
CaS	2.38	2.64
Inert		

GAS / REGENERATOR

	(9)	GAS (10)	(11)	(12)
CH₄, Mol %	13.10(13.05)	.06	12.00	
	57.15(57.31)	2.50		
	17.13(16.72)			
	9.89(10.20)	29.51	88.00	79.00
	2.73(2.72)	87.93		21.00

* **NOTE:** The gasifier bed temperature was 1490°F. The bed level was somewhat low in this run, such that the surging bed did not cover the stream of hot acceptor entering the gasifier. The result was that the gas leaving the gasifier was heated to 1520°F, as measured by thermocouples above the entering acceptor stream. The numbers in parentheses are the flows and compositions at the top of the bed.

Table 5-18. HEAT AND MATERIAL BALANCE – RUN 33B 1600 HOURS
FEBRUARY 15 TO 0800 HOURS FEBRUARY 17, 1976
VELVA LIGNITE SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Coal Feed(1)	2,470		400	255,500	29,086,900
Acceptor(8)	11,599		1840	4,473,000	
Boot Gas			1440		
Recycle(9)					
Steam	1,384	9,040		268,700	
CO₂	113	29,120		2,406,300	
		970		40,400	
Ring Gas			1500		
Steam	1,233	25,940		2,184,200	
Air	465	6,110		173,400	
Purge Gas			60		
Recycle(9)	250	2,600			
Inert(11)	71	3,160			
N₂		960			
Subtotal	17,585			9,801,500	29,086,900
Heats of Reaction					
CaO + CO₂ = CaCO₃ 32.445 Mols at 76,200 Btu/Mol				2,472,300	2,155,600
Total	17,585			12,273,800	

Output
Char

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
To Regenerator(2)	655		1515	348,400	7,580,600
Cyclone Loss(3)	206		1565	113,000	2,155,600
Acceptor(7)			1515		
To Regenerator	12,993		1565	4,302,300	
Gas	2,432	64,430(64,649)*		2,108,600	21,626,600
Product(9)		11,640(11,681)		381,000	
Recycle(9)	1,279	28,900(26,634)		2,311,900	
Steam	5.4	60		2,300	38,400
H₂S	13	285		13,000	123,800
NH₃					
Subtotal	17,585.4			9,579,300	31,525,000
Heats of Reaction					
CaO + S = CaS + O 0.297 Mols at 196,540 Btu/Mol				2,436,100	
Heat Loss				58,400	
Total	17,585.4			12,273,800	

COAL OR CHAR	(1)	(2)	(3)	(4)	(5)
H, Wt %, Dry	4.87	.70	.94		2.03
C	68.69	77.59	68.09	6.44	75.62
N	.71	0.45	.30		.68
O	18.46				7.92
S	0.59				1.41
Ash				79.93	
Oxides	6.66	11.03	20.03	11.63	12.34
CaS		0.223	.720		
CaCO₃		10.01	9.92		
Wt %, Moisture					.55

REGENERATOR

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(2)	655		1515	346,400	7,580,600
Auxiliary Fuel(5)	80	9	60		930,900
Moisture	0.4				
Acceptor					
From Gasifier(7)	12,993		1515	4,302,300	
Make-up(6)	560		60		
Ring Gas			840		
Steam	6,086	79,950		1,187,300	
Recycle(10)		12,220		200,700	
Moisture	26	540		36,300	
Acceptor Lift Gas					
Recycle(10)	15	54,420	1350	1,556,600	
Moisture		320		25,600	
Char Lift Gas			780		
Inert(11)	553	7,000		96,900	
Recycle(10)		3,250		49,000	
Moisture	0.9	20		1,300	
Purge Gas			60		
Recycle(10)	58	1,570			
Inert(11)	7.9	710			
N₂		110			
Subtotal	21,033.2			7,802,400	8,511,500
Heats of Reaction (Input - Output ex-Acceptor)					
CaS + O = CaO + S 0.058 Mols at 196,540 Btu/Mol				11,400	
Total	21,033.2			15,309,200	

Output
Char

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(4)	135		1840	62,000	162,000
Acceptor(8)			1840		
To Gasifier	11,599			4,473,000	
Overhead	48			18,300	
Reject	269			103,700	
Gas			1840		
Flue(10)	8,883	102,960		4,238,200	845,500
Recycle(10)	94	71,460		2,940,100	
Steam	1.3	1,990		185,700	
COS	0.5	6		500	5,100
H₂S	3.7	5.5		300	3,500
SO₂		22		1,300	
Subtotal	21,033.5			12,021,100	1,016,100
Heats of Reaction					
MgCO₃ = MgO + CO₂ 0.151 Mols at 45,000 Btu/Mol				6,800	
CaCO₃ = CaO + CO₃ 37.623 Mols at 76,200 Btu/Mol				2,866,900	
Heat Loss				414,400	
Total	21,033.5			15,309,200	

ACCEPTOR	(7)	(8)
CaO, Wt %	71.46	95.44
CaCO₃	24.33	
MgO	1.72	1.92
MgCO₃	.142	
CaS	2.35	2.64
Inert		

	(6)		
	(6)		
H	96.24		
C			
O	2.27		
	1.49		

GAS	(9)	(10)	(11)	(12)
CH₄, Mol %	11.90(11.86)*	.06		
H₂	52.35(52.51)	2.50		
CO	14.09(13.70)	29.36	12.00	
CO₂	6.29 (8.60)	68.08	88.00	79.00
N₂	13.37(13.33)			21.00
O₂				

* NOTE: The gasifier bed temperature was 1515°F. The bed level was somewhat low in this run, such that the surging bed did not cover the stream of hot acceptor entering the gasifier. The result was that the gas leaving the gasifier was heated to 1565°F, as measured by thermocouples above the entering acceptor stream. The numbers in parentheses are the flows and compositions at the top of the bed.

Table 5-19. HEAT AND MATERIAL BALANCE - RUN 38C 0000 HOURS
AUGUST 26 TO 0700 AUGUST 27, 1976 WYODAK
SUBBITUMINOUS COAL SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Coal Feed(1)	2,690		255	140,400	29,228,800
Acceptor(8)	10,204		1845 1425	3,946,700	
Boot Gas					
Recycle(9)	1,573	10,600		312,900	
Steam		33,100	1500	2,721,100	
Ring Gas					
Steam	1,066	22,430	60	1,888,900	
Purge					
Recycle(9)		3,450			
Inert(11)	142	1,800			
N₂	90	1,215			
Subtotal	15,765			9,010,000	29,228,800
Heats of Reaction					
CaO + CO₂ = CaCO₃ 36.05 Mols at 76,200 Btu/Mol				2,747,400	
Total	15,765			11,757,400	
Output					
Char					
To Regenerator(2)	675		1490	340,900	7,204,300
Cyclone Losses(3)	206			102,600	2,068,700
Acceptor					
To Regenerator(7)	11,747		1490	3,865,800	
Gas					
Product(9)	2,004	60,760	1490	1,888,900	22,576,500
Recycle(9)		14,050		436,600	
Steam	1,109	23,330		1,958,500	
H₂S	5.3	59		2,200	37,700
NH₃	19	424		18,100	184,200
Subtotal	15,765.3			8,613,600	32,071,400
Heats of Reaction					
CaO + 6 = CaS + O 0.525 Mols at 196,540 Btu/Mol				2,842,600	
Heat of Combustion (Output - Input ex-Acceptor)				103,200	
Heat Loss				198,000	
Total	15,765.3			11,757,400	

REGENERATOR

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char(2)	675		1490	340,900	7,204,300
Aux. Fuel(5)	182		60		1,921,800
Moisture	2	40			
Acceptor					
From Gasifier(7)	11,747		1490	3,865,800	
Make-up(6)	700		60		
Ring Gas					
Air(12)	6,405	84,140	840	1,249,500	
Moisture	23	491		33,100	
Acceptor Lift Gas					
Recycle(10)		53,860	1350	1,543,800	
Moisture	15	314		25,200	
Char Lift Gas					
Inert(11)	553	7,000	780	96,900	
Recycle(10)		2,970		44,900	
Moisture	1	17		1,100	
Purge Gas					
Recycle(10)		2,690	60		
Inert(1)	55	700			
N₂	10	135			
Subtotal	20,368			7,201,200	9,126,100
Heats of Reaction (Input - Output ex-Acceptor)					
CaS + O = CaO + S .08 Mols at 196,540 Btu/Mol				7,827,100	
				15,000	
Total	20,368			15,043,300	
Output					
Char(4)	189		1845	90,200	173,600
Acceptor(8)					
To Gasifier	10,204		1845	3,946,700	
Overhead	59			22,900	
Reject	338			130,000	
Gas					
Flue(10)	9,458	109,460	1845	4,526,600	1,116,500
Recycle(10)		59,520		2,461,600	
Steam	101	2,117		198,300	
CO6	1.3	8.1		500	
H₂S	0.5	6.0		300	5,100
SO₂	8.9	52.6		3,100	3,800
Subtotal	20,367.7			11,380,200	1,299,000
Heats of Reaction					
MgCO₃ = MgO + CO₂ 0.19 Mols at 45,000 Btu/Mol				8,500	
CaCO₃ = CaO + CO₂ 42.52 Mols at 76,200 Btu/Mol				3,240,200	
Heat Loss				414,400	
Total	20,367.7			15,043,300	

LIGNITE OR CHAR

	(1)	(2)	(3)	(4)	(5)		
H, Wt %, Dry	4.15	.81	.61	6.12	1.66	CaO, Wt % Dry	
C	65.11	71.68	67.08		68.84	CaCO₃	
N	.97	.41	.36		.85	MgO	
O	21.59				7.20	MgCO₃	
S	.81				1.75	CaS	19.70
						Inert	1.75
Ash	7.37	13.70	17.91	78.00	19.70		
Oxides				14.88			
CaS		.432	1.283				
CaCO₃		13.17	12.76				
Wt %, Moisture					1.05		

ACCEPTOR

	(6)	(7)	(8)
CaO	96.24	66.03	95.44
CaCO₃		29.74	
MgO	2.27	1.67	1.92
MgCO₃		.275	
CaS	1.49	2.28	2.64

GAS

	(9)	(10)	(11)	(12)
CH₄, Mol %	13.00	.07		
H₂	58.72	3.10		
CO	15.36	29.73	12.00	79.00
CO₂	8.18	67.10	88.00	21.00
N₂	4.76			

Table 5-20. HEAT AND MATERIAL BALANCE - RUN 39 1900 TO 2300 HOURS SEPTEMBER 29, 1976 GLENHAROLD LIGNITE SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Coal Feed(1)	2,530		330	135,700	27,671,100
Acceptor(6)	8,703		1835	2,577,200	
Bed Gas			140u		
Recycle(9)	1,029	8,860		257,800	
Steam		21,650		1,766,200	
Ring Gas	1,315	27,670	1500	2,329,900	5,629,000
Air(12)	863	11,330		321,400	2,905,900
Purge Gas			60		
Recycle(9)	70	2,050			
Inert(11)	279	880			
H₂		3,780			
Subtotal	12,769			7,448,200	27,671,100
Heats of Reaction CaO + CO₂ = CaCO₃ 22.454 Mols at 78,200 Btu/Mol				1,711,000	
Total	12,769			9,159,200	27,671,100

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char			1480		
To Regenerator(2)	583			282,300	5,629,000
Cyclone Loss(3)	327			157,400	2,905,900
Acceptor(7)	7,564		1480	2,430,500	
Gas			1480		
Product(9)	3,051	67,860		2,105,500	20,541,200
Recycle(9)	1,137	10,910		338,400	
Steam		23,910		2,001,000	
H₂S	7.5	83		3,000	53,000
N₂	19.5	431		18,300	187,300
Subtotal	12,769			7,399,100	29,316,300
Heats of Reaction					
Heat of Combustion (Output - Input ex-Acceptor) CaO + S = CaS + O 0.555 Mols at 196,540 Btu/Mol					
Net Loss				1,643,200	
Total	12,769			110,900	
				196,200	
				9,159,200	

REGENERATOR

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(2)	583		1480	282,300	5,629,000
Auxiliary Fuel(5)	262	510	60		2,826,500
Moisture	24				
Acceptor			1480		
From Gasifier(7)	7,564		60	2,493,200	
Makeup(6)	840		800		
Ring Gas					
Air(12)	5,567	73,130		1,028,400	
Recycle(10)		13,000		199,200	
Moisture	24	503		33,500	
Acceptor Lift Gas			1355		
Recycle(10)					
Moisture	15	53,870		1,527,500	
Char Lift Gas		314		25,300	
Recycle(10)	553	7,000	770	95,500	
Inert(11)		3,080		45,200	
Moisture	1	18		1,200	
Purge Gas					
Recycle(10)	33	540			
Inert(11)	31	430			
H₂		430			
Subtotal	15,597			5,731,300	8,455,500
Heats of Reaction (Input ex-Acceptor)					
Heat of Combustion (Input - Output ex-Acceptor) CaS + O = CaO + S 0.132 Mols at 196,540 Btu/Mol				8,855,500	
Total	15,597			25,900	
				12,612,700	

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(6)					
Acceptor(6)	211		1835	94,800	135,700
To Gasifier			1835		
Overhead	8,703	94,320		2,577,200	
Reject	71	70,450		27,400	
	403	3,840		155,100	
Gas			1835		
Flue	8,018			3,815,900	1,433,200
Recycle	183			2,851,600	
Steam				350,800	
CO₂	1.1	8.8		400	
H₂O	1.0	10.8		300	4,300
SO₂	7.9	46.6		2,700	6,600
Subtotal	15,597			9,864,400	1,600,000
Heats of Reaction					
MgO = MgO + CO₂ 0.227 Mols at 45,000 Btu/Mol				10,200	
CaCO₃ = CaO + CO₂ 30.233 Mols at 78,200 Btu/Mol				2,303,700	
Net Loss				414,400	
Total	15,597			12,612,700	

H, Wt % Dry	LIGNITE OR CHAR (1)	(2)	(3)	(4)	(5)	ACCEPTOR (7)	(8)		GAS (9)	(10)	(11)	(12)
H	4.46	.57	.73		4.25	67.31	55.44	(6)	11.30	.23		
C	64.06	64.69	58.72	5.18	64.58	28.21		56.24	43.44	4.50		
N	1.08	.42	.42		.80	1.68	1.52		14.73	26.59	12.00	
O	17.77				23.57			2.27	10.49	68.69	88.00	
S	1.03		.65		.65	0.358			20.04			
Ash						2.30	2.64	1.49				
Oxides	11.63	24.77	29.34	61.25	6.34							79.00
CaS		1.391	1.49	13.67								21.00
CaCO₃		8.26	9.10									
Inert												
Wt %, Moisture					9.28							

Table 5-21. HEAT AND MATERIAL BALANCE – RUN 40B 0800 TO 1600
HOURS NOVEMBER 18, 1976 TEXAS LIGNITE SYSTEM PRESSURE
150 PSIG

111

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Coal Feed(1)	2,140		340	173,200	24,905,800
Acceptor(8)	19,618		1843	8,570,900	
Boot Gas					
Steam	1,711	36,000	1520	3,050,900	
CO₂	108	933	1520	41,500	
Ring Gas					
Steam	765	16,100	1495	1,353,700	
Recycle(9)			60		
Purge Gas					
Recycle(9)	27	2,480			
Inert Gas(11)	143	340			
Nitrogen		1,940			
Subtotal	24,512			13,190,200	24,905,800
Heats of Reaction					
CaO + CO₂ = CaCO₃ 23.00 Mols at 76,200 Btu/Mol				1,905,000	
Total	24,512			15,095,200	
Output					
Char					
To Regenerator(2)	480		1528	246,100	4,820,100
Cyclone Loss(3)	162		1560	85,700	1,556,000
Gas					
Product(9)	2,099	59,250(59,407)*	1528	1,945,600	21,404,500
Recycle(9)	1,052	2,480 (2,486)	1560	81,300	
Steam		22,140(21,977)	1560	1,899,700	
H₂S	5	54		2,100	34,200
NH₃	15	320		14,700	140,500
Acceptor(7)	20,699		1528	7,479,400	
Subtotal	24,512			11,754,600	27,955,300
Heats of Reaction					
Heat of Combustion (Output - Input ex-Acceptor)				3,049,300	
CaO + S = CaS + O .474 Mols at 196,540 Btu/Mol				93,100	
Heat Loss				198,000	
Total	24,512			15,095,200	

COAL OR CHAR

	(1)	(2)	(3)	(4)
H, Wt %, Dry				
H	4.73	0.62	0.74	5.92
C	67.10	67.27	63.54	
N	0.93	0.27	0.35	
O	17.76			
S	0.92			
Ash	8.56			
Oxides	23.55	.244	20.77	79.28
CaS			1.711	14.80
CaCO₃		8.051	.895	

REGENERATOR

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char(2)	480		1528	246,100	4,820,100
Aux. Fuel(5)	304		60		3,538,000
Acceptor					
From Gasifier(7)	20,699		1528	7,479,400	
Makeup(6)	560		60		
Ring Gas					
Air(12)	1,483	19,490	770	262,500	
Recycle Gas(10)		17,920		263,300	
Moisture	10	220		14,400	
Acceptor Lift Gas					
Air(12)	4,422	58,100	780	794,100	
Moisture	16	340		22,400	
Char Lift Gas					
Inert Gas(11)	553	7,000	770	95,500	
Recycle Gas(10)		2,670		39,200	
Moisture	0.7	16		1,000	
Purge Gas					
Recycle Gas(10)		3,040	60		
Inert(11)	47	600			
Nitrogen	67	910			
Subtotal	28,642			9,217,900	8,358,100
Heats of Reaction (Input - Output ex-Acceptor)					
CaS + O = CaO + S 0.07 Mols at 196,540 Btu/Mol				13,600	
Total	28,642			16,760,500	
Output					
Char(4)	178		1843	80,400	150,200
Acceptor(8)					
To Gasifier	19,618		1843	8,570,900	
Overhead	61			26,700	
Reject	245			106,900	
Gas					
Flue Gas(10)	8,355	97,860	1843	3,993,300	669,000
Recycle(10)		26,630		964,200	
Steam	176	3,700		346,400	
COS	0.8	5		300	3,300
H₂S	0.9	10		500	6,600
SO₂	7.4	44		2,600	
Subtotal	28,642			14,092,200	829,100
Heats of Reaction					
MgCO₃ = MgO + CO₂ 3.24 Mols at 45,000 Btu/Mol				145,600	
CaCO₃ = CaO + CO₂ 27.33 Mols at 76,200 Btu/Mol				2,082,500	
Heat Loss				440,200	
Total	28,642			16,760,500	

ACCEPTOR

	(6)	(7)	(8)
CaO, Wt %		37.36	46.51
CaCO₃	15.34	11.801	
MgO	48.72	40.41	42.64
MgCO₃		.146	
CaS	5.94	10.28	10.85

GAS

	(9)	(10)	(11)	(12)
CH₄, Mol %	11.90(11.87)*	0.13		
H₂	56.64(56.75)	2.00		
CO	17.70(17.40)	27.41	12.00	
CO₂	9.84(10.07)	70.46	88.00	79.00
N₂	3.92 (3.91)			21.00
O₂				

* NOTE: The gasifier bed temperature was 1528°F. The bed level was somewhat low in this run, such that the surging bed did not cover the stream of hot acceptor entering the gasifier. The result was that the gas leaving the gasifier was heated to 1560°F, as measured by thermocouples above the entering acceptor stream. The numbers in parentheses are the flows and compositions at the top of the bed.

Table 5-22. HEAT AND MATERIAL BALANCE - RUN 45 0700 HOURS
JUNE 6 TO 0700 HOURS JUNE 7, 1977 WYODAK
SUBBITUMINOUS COAL SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Coal Feed(1)	2,885		349	242,900	31,725,000
Acceptor(8)	16,965		1890	6,738,500	
Soot Gas			1460		
Recycle(9)		5,060		156,400	
Steam	2,164	45,530		3,785,900	
CO2	120	1,030		43,600	
Ring Gas			1500		
Steam	903	19,000		1,600,100	
Purge Gas			60		
Recycle(9)		2,440			
Inert(11)	22	275			
N2	299	4,050			
Subtotal	23,358			12,567,400	31,725,000
Heats of Reaction					
CaO + CO2 = CaCO3	31.72 Mols at 76,200 Btu/Mol			2,417,400	
Total	23,358			14,984,800	

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char					
To Regenerator(2)	729		1490	372,300	7,787,300
Cyclone Loss(3)	143		1500	73,400	1,462,900
Acceptor					
To Regeneration(7)	13,300		1490	5,833,100	
Gas			1500		
Product(9)	2,771	72,350(72,420)*		2,306,200	25,689,700
Recycle(9)	1,386	7,500 (7,510)		239,200	
Steam		29,155(29,076)		2,455,300	
H2S	11	125		4,600	
NH3	18	412		17,800	
Subtotal	23,358			11,301,900	35,199,100
Heats of Combustion (Output - Input ex-Acceptor)				80,000	179,200
CaO + S = CaS + O	.055 Mols at 196,540 Btu/Mol				
Heat Loss				198,000	
Total	23,358			14,984,800	

LIGNITE OR CHAR

	(1)	(2)	(3)	(4)	(5)
H, Wt %, Dry	4.30	.70	.71	6.89	4.30
C	65.93	71.29	68.00		65.93
N	.88	.38	.35		.88
O	22.11				22.11
S	.43				.43
Ash					
Oxides	6.35	12.10	9.73	92.68	6.35
CaS		.128	.967	.43	
CaCO3		15.40	20.24		

REGENERATOR

Input	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(2)	729		1490	372,300	7,787,300
Aux. Fuel(5)	101		60	-	1,110,600
Acceptor					
From Gasifier(7)	18,300		1490	5,833,100	
Makeup(6)	270		60		
Ring Gas			767		
Air(12)	1,920	25,220		338,300	
Recycle(10)		13,770		201,800	
Moisture	11	227		15,000	
Acceptor Lift Gas			785		
Air(12)	4,306	56,570		778,800	
Moisture	16	330		21,900	
Char Lift Gas			790		
Inert(11)	553	7,000		98,300	
Recycle(10)		6,260		95,000	
Moisture	1.7	37		2,400	
Purge			60		
Recycle(10)	66	2,475			
Inert(11)	33.3	830			
N2		450			
Subtotal	26,307			7,756,900	8,897,900
Heats of Reaction				7,701,700	
Heat of Combustion (Input - Output ex-Acceptor)				5,300	
CaS + O = CaO + 6	0.03 Mols at 196,540 Btu/Mol				
Total	26,307			15,466,900	

Output	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Char(4)	170		1890	82,100	167,000
Acceptor(8)			1890		
To Gasifier	16,965			6,738,500	
Overhead	23			9,100	
Reject	130			51,500	
Gas			1890		
Flue(10)	8,910	104,110		4,385,700	1,017,500
Recycle(10)		22,505		948,000	
Steam	107	2,258		214,300	
COS	1.1	6.7		400	
H2S	0.6	7.1		300	
SO2	0.3	1.5		100	
Subtotal	26,307			12,430,000	1,193,200
Heats of Reaction					
MgCO3 = MgO + CO2	0.07 Mols at 45,000 Btu/Mol			3,300	
CaCO3 = CaO + CO2	34.03 Mols at 76,200 Btu/Mol			2,593,400	
Heat Loss				440,200	
Total	26,307			15,466,900	

ACCEPTOR

	(6)	(7)	(8)
CaO, Wt %, Dry	96.24	79.19	95.44
CaCO3		16.59	
MgO	48.27	1.78	1.92
MgCO3			
CaS			
Inert	1.49	2.44	2.64

GAS

	(9)	(10)	(11)	(12)
CH4, Mol %	12.73(12.72)*	.13	12.00	79.00
H2	53.05(53.14)	2.94	88.00	21.00
CO	16.81(16.69)	27.79		
CO2	11.35(11.44)	69.17		
N2	6.06(6.05)			
O2				

Table 5-23. HEAT AND MATERIAL BALANCE - RUN 46C 1500 TO 2300
HOURS, AUGUST 9, 1977 VELVA LIGNITE SYSTEM
PRESSURE 190 PSIG

* NOTE: The gasifier bed temperature was 1490°F. The bed level was somewhat low in this run, such that the surging bed did not cover the stream of hot acceptor entering the gasifier. The result was that the gas leaving the gasifier was heated to 1500°F, as measured by thermocouples above the entering acceptor stream. The numbers in parentheses are the flows and compositions at the top of the bed.

Basis: 1 hour
Datum: 60°F, liquid water

GASIFIER

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Lignite(1)	2,720		350	230,000	30,132,500
Acceptor(8)	22,051		1860	8,752,600	
Boot Gas					
Steam	1,925	40,500	1450	3,357,000	
CO₃	110	950	1450	39,900	
Ring Gas					
Steam	618	13,000	1470	1,084,400	
Purge Gas					
Recycle(9)	24	2,525	60		
Inert(11)	233	3,150	60		
Nitrogen			60		
Subtotal	27,681			13,463,900	30,132,500
Heats of Reaction:					
CaO + CO₃ = CaCO₃ 32.296 Mols at 76,300 Btu/Mol				2,460,900	
Total	27,681			15,924,800	
Output					
Char					
To Regenerator(2)	669		1510	350,600	7,267,000
Cyclone Loss(3)	171		1530	39,600	1,769,600
Acceptor					
To Regenerator(7)	23,422		1510	7,622,000	
Gas					
Product(9)	2,455	69,000(69,131)*	1530	2,189,200	24,493,400
Recycle(9)		2,525(2,529)	1530	80,100	
Steam	939	19,750(19,629)		1,679,000	
H₂S	4	49		1,800	31,400
HB	21	468		20,700	203,500
Subtotal	27,681			12,033,000	33,764,900
Heats of Reaction:					
CaO + S = CaS + O .313 Mols at 196,540 Btu/Mol				3,632,400	
Heat Loss				61,400	198,500
Total	27,681			15,924,800	

REGENERATOR

	Lbs	SCF	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char(2)	669		1510	350,600	7,267,000
Aux. Fuel(5)	153		60		1,695,000
Acceptor					
From Gasifier(7)	23,422		1510	7,622,000	
Makeup(6)	268		60		
Ring Gas			741		
Air(12)	1,587	20,850		269,000	
Moisture	6	126		7,900	
Acceptor Lift Gas					
Air(12)	4,350	57,150	786	787,900	
Moisture	16	337	786	22,100	
Char Lift Gas					
Inert(11)	553	7,000	760	94,100	
Recycle(10)		3,500		50,000	
Moisture	1	20		1,300	
Purge Gas			60		
Recycle(10)		2,480			
Inert(11)		1,100			
Nitrogen		1,350			
Subtotal	31,212			9,204,300	8,962,000
Heats of Reaction (Input - Output ex-Acceptor)					
CaS + O = CaO + S .006 Mols at 196,540 Btu/Mol				1,100	
Total	31,212			16,455,400	
Output					
Char(4)	163		1860	76,000	200,100
Acceptor(8)					
To Gasifier	22,051		1860	8,752,600	
Overhead	39			15,500	
Reject	222			88,000	
Gas					
Flue Gas(10)	8,613	101,500	1860	4,164,700	1,505,300
Recycle(10)	6,000	6,000		244,400	
Steam	117	2,470		231,900	
COS	.7	5		300	
H₂S	.6	7		300	3,000
SO₂	5.7	34		2,000	4,600
Subtotal	31,212			13,575,700	1,713,000
Heats of Reaction					
CaCO₃ = CaO + CO₂ 32.015 Mols at 76,200 Btu/Mol				- 2,439,500	
Heat Loss				440,200	
Total	31,212			16,455,400	

LIGNITE OR CHAR

	(1)	(2)	(3)	(4)	(5)
H, Wt %, Dry	4.33	.77	.7		4.33
C	66.37	72.28	69.22		66.37
N	1.06	.35	.38	8.60	1.06
O	21.36				21.36
S	.52				.52
Ash	6.36	11.91	12.31	78.93	6.36
Oxides		.18	.99	12.47	
CaS					
CaCO₃		14.51	16.40		

ACCEPTOR

	(6)	(7)	(8)
CaO, Wt %, Dry	84.41	74.19	86.76
CaCO₃		13.267	
MgO	3.06	2.94	3.12
MgCO₃		.084	
CaS	9.83	9.52	10.12
Inert	2.71		
SO₂			

GAS

	(9)	GAS (10)	(11)	(12)
CH₄, Mol %	11.00(10.98)*	.21	12.00	79.00
H₂	56.17(56.25)	4.40	83.00	21.00
CO	19.04(18.84)	26.27		
CO₂	8.68(8.83)	69.12		
N₂	5.11(5.10)			
O₂				

NOTE: The gasifier bed temperature was 1510°F. The bed level was somewhat low in this run, such that the surging bed did not cover the stream of hot acceptor entering the gasifier. The result was that the gas leaving the gasifier was heated to 1530°F, as measured by thermocouples above the entering acceptor stream. The numbers in parentheses are the flows and compositions at the top of the bed.

* The numbers in parentheses are the flows and compositions at the top of the bed.

Table 5-24. HEAT AND MATERIAL BALANCE - RUN 47B 1230 HOURS
SEPTEMBER 29 to 0700 HOURS OCTOBER 1, 1977
VELVA LIGNITE - RECONSTITUTED ACCEPTOR SYSTEM
PRESSURE 150 PSIG

	Run 21-I	Run 21-II	Run 21-III	Run 26B	Run 28B	Run 33B	Run 38C	Run 39	Run 40B	Run 45	Run 46C	Run 47B
Coal	Velva Lignite	Velva Lignite	Velva Lignite	Velva Lignite	Velva Lignite	Velva Lignite	Wyodak Subbit.	Glenharold Lignite	Texas Lignite	Wyodak Subbit.	Velva Lignite	Velva Lignite
Acceptor	Dolomite	Dolomite	Dolomite	Dolomite	Limestone	Limestone	Limestone	Limestone	Limestone	Dolomite	Limestone	Reconst. Limestone
Run Conditions												
Bed Temperature, °F												
Gasifier	1480	1480	1500	1495	1490	1490	1515	1490	1480	1528	1490	1510
Regenerator	1850	1860	1850	1840	1840	1845	1840	1845	1835	1843	1890	1860
Coal Feedrate, lb/hr	2550	2600	2500	2450	2570	2770	2470	2690	2530	2140	2885	2720
Circulation Rate, lb/hr	11,860	11,510	10,840	10,680	14,280	15,040	13,000	11,750	7,660	20,700	18,300	23,420
Acceptor Activity	0.320	0.343	0.300	0.370	0.132	0.142	0.160	0.201	0.190	0.150	0.105	0.091
Fuel Char to Regenerator, lb/hr	736	768	704	625	537	710	655	675	583	480	729	669
Gasifier Overhead Solids, lb/hr	113.7	105.5	110.6	100.3	121.9	130.9	208.3	206.5	326.7	162.5	143.3	170.6
Char Bed Reject, lb/hr	0	0	0	75	114	0	0	0	0	0	0	0
Auxiliary Fuel, lb/hr	0	0	0	105.8	191.9	66	79.6	182.1	261.7	304	101	153
Total Gasifier Steam, SCFH	59,070	59,780	53,090	55,080	54,000	56,400	55,060	55,530	49,320	52,100	64,530	53,500
Gasifier Air, SCFH	0	0	0	0	0	0	6114	0	11,334	0	0	0
Recycle Gas to Gasifier Boot, SCFH	12,026	12,797	6959	14,596	0	0	9036	10,595	8857	0	5062	0
Regenerator Air (measured), SCFH	77,000	81,000	72,500	77,160	78,750	84,860	82,500	86,660	77,000	80,550	84,400	78,380
Regenerator Air (as calculated by process model), SCFH	75,400	78,000	70,030	76,720	76,520	81,800	80,420	84,630	73,560	78,040	82,270	78,450
% Difference	-2.1	-3.7	-3.4	-0.6	-2.8	-3.5	-2.5	-2.3	-4.5	-3.1	-2.5	+0.1
Results Which are not Stated Explicitly in Tables 5-13 Through 5-24												
% Steam Conversion	50.4	49.0	50.9	55.3	58.6	58.0	51.1	58.0	51.5	57.5	54.8	63.1
% Fixed Carbon Gasified	52.3	51.0	53.2	53.7	55.8	54.6	50.1	52.9	53.2	61.0	57.1	56.1
Carbon in Char Bed, lb	656	652	648	660	727	754	651	699	646	667	823	768
Carbon Gasified, lb	2460	2520	1580	2480	2730	2750	2770	2740	2430	2280	3190	2510
Mol CH_4 Produced per atom carbon gasified	0.244	0.243	0.198	0.227	0.225	0.224	0.232	0.222	0.231	0.221	0.227	0.200
Mol CH_4 in Raw Gas per mol CH_4 in SNG	.450	.450	--	.414	.416	.417	--	.416	--	.394	.425	.368
% Acceptor Duty met by Recarbonation Reaction	84.4	85.8	84.8	92.7	84.0	86.2	93.4	97.0	95.2	63.0	71.8	67.7
Net Heat of Reaction per Atom of Carbon Gasified, Btu	32,650	31,270	26,120	33,130	31,380	31,470	28,640	31,330	17,840	37,380	32,580	36,860
Mols $CaCO_3$ Formed per atom carbon gasified	0.331	0.341	0.298	0.359	0.308	0.329	0.362	0.371	0.242	0.290	0.283	0.310
Mols $CaCO_3$ Formed per 100 lb coal feed gasified	1.15	1.16	1.04	1.28	1.14	1.19	1.28	1.30	0.86	1.14	1.05	1.19
HHV Auxiliary Fuel per HHV gasifier char loss	--	--	--	0.717	0.874	0.504	0.432	0.929	0.973	2.27	0.759	0.958
HHV Auxiliary Fuel per HHV total fuel to regenerator	--	--	--	0.153	0.268	0.078	0.109	0.211	0.334	0.423	0.125	0.189

HHV = Heat of combustion; moisture free, 60°F, liquid water basis.

Table 5-25. SUMMARIZED RUN CONDITIONS AND RESULTS

	Run 21 (Balance I)		Run 21 (Balance II)		Run 21 (Balance III)		Run 26B	
	Btu/hr	Percent	Btu/hr	Percent	Btu/hr	Percent	Btu/hr	Percent
In								
Coal Feed, heat of combustion	27,800,000	100.0	28,305,400	100.0	27,245,100	100.0	27,597,700	100.0
Out								
Heats of Combustion								
Gasifier Streams								
Product Gas	21,439,100	77.1	21,396,500	75.6	20,704,400	76.0	21,656,900	78.5
Net Char(1)	1,097,600	4.0	1,024,100	3.6	1,020,400	3.8	487,900	1.8
$NH_3 + H_2S$	242,400	0.9	235,700	0.8	228,800	0.9	211,000	0.8
Regenerator Streams								
Flue Gas + H_2S + COS	645,100	2.3	999,700	3.5	901,700	3.3	725,300	2.6
Overhead Ash	149,400	0.5	159,100	0.6	143,000	0.5	152,100	0.5
Net Heats of Reaction								
$MgCO_3 = MgO + CO_2$	140,200	0.5	140,200	0.5	140,200	0.5	140,000	0.5
$CaCO_3 = CaO + CO_2$	139,100	0.5	135,900	0.5	142,400	0.5	121,100	0.4
$CaO + S = CaS + O$	33,000	0.1	31,200	0.1	36,300	0.1	44,400	0.2
Sensible Heats								
Outlet Streams - Inlet Streams	3,311,100	11.9	3,580,000	12.7	3,324,900	12.2	3,456,000	12.3
Heat Losses								
Gasifier	198,000	0.7	198,000	0.7	198,000	0.7	198,000	0.7
Regenerator	405,000	1.5	405,000	1.4	405,000	1.5	405,000	1.5
Total	27,800,000	100.0	28,305,400	100.0	27,245,100	100.0	25,597,700	100.0

(1) Heat of combustion, net char = heat of combustion of all gasifier char losses - heat of combustion of auxiliary fuel stream.

Table 5-26. SUMMARIZED HEAT BALANCE

		Run 28B		Run 33B		Run 38C		Run 39	
		Btu/hr	Percent	Btu/hr	Percent	Btu/hr	Percent	Btu/hr	Percent
In									
Coal Feed, heat of combustion		28,912,500	100.0	30,608,500	100.0	29,086,900	100.0	29,228,800	100.0
Out									
Heats of Combustion									
Gasifier Streams									
Product Gas		23,053,200	79.7	24,144,200	78.9	21,626,600	74.3	22,576,500	77.2
Net Char(1)		317,900	1.1	669,800	2.2	1,224,700	4.2	146,900	0.5
$NH_2 + H_2S$		213,500	0.7	218,000	0.7	162,200	0.6	221,900	0.8
Regenerator Streams									
Flue Gas + H_2S + COS		980,300	3.4	873,000	2.8	854,100	2.9	1,125,400	3.9
Overhead Ash		156,400	0.5	165,400	0.5	162,000	0.6	173,600	0.6
Net Heats of Reaction									
$MgCO_3 = MgO + CO_2$		6,800	< 0.1	6,800	< 0.1	6,800	< 0.1	8,500	< 0.1
$CaCO_2 = CaO + CO_2$		338,300	1.2	395,600	1.3	394,600	1.4	492,800	1.7
$CaO + S = CaS + O$		44,400	0.2	37,000	0.1	47,000	0.2	88,200	0.3
Sensible Heats									
Outlet Streams - Inlet Streams		3,198,700	11.1	3,486,300	11.4	3,996,500	13.7	3,782,600	12.9
Heat Losses									
Gasifier		198,000	0.7	198,000	0.7	198,000	0.7	198,000	0.7
Regenerator		405,000	1.4	414,400	1.4	414,400	1.4	414,400	1.4
	Total	28,912,500	100.0	30,608,500	100.0	29,086,900	100.0	29,228,800	100.0

(1) Heat of combustion, net char = heat of combustion of all gasifier char losses - heat of combustion of auxiliary fuel stream.

Table 5-26.   SUMMARIZED HEAT BALANCE (continued)

117

	Run 40B		Run 45		Run 46C		Run 47B	
	Btu/hr	Percent	Btu/hr	Percent	Btu/hr	Percent	Btu/hr	Percent
In								
Coal Feed, heat of combustion	27,871,100	100.0	24,905,800	92.6	31,725,000	100.0	30,132,500	99.9
Net Char,(1) heat of combustion			1,982,000	7.4				
$CaCO_3$ = CaO + CO_2, net heat of reaction							21,400	0.1
Total	27,871,100		26,887,800	100.0	31,725,000		30,153,900	100.0
Out								
Heats of Combustion								
Gasifier Streams								
Product Gas	20,541,200	73.7	21,404,500	79.6	25,689,700	81.0	24,493,400	81.2
Net Char(1)	79,100	0.3			352,300	1.1	74,200	0.2
NH_3 + H_2S	240,500	0.9	174,700	0.7	259,200	0.8	234,900	0.8
Regenerator Streams								
Flue Gas + H_2S + COS	1,444,300	5.2	678,900	2.5	1,026,200	3.2	1,512,900	5.0
Overhead Ash	155,700	0.6	150,200	0.6	167,000	0.5	200,100	0.7
Net Heats of Reaction								
$MgCO_3$ = MgO + CO_2	10,200	< 0.1	145,600	0.5	3,300	< 0.1		
$CaCO_3$ = CaO + CO_2	592,700	2.1	177,500	0.7	176,000	0.6	60,300	0.2
CaO + S = CaS + O	91,000	0.3	79,500	0.3	5,500	< 0.1		
Sensible Heats								
Outlet Streams - Inlet Streams	4,104,000	14.7	3,438,700	12.8	3,407,600	10.8	2,939,900	9.8
Heat Losses								
Gasifier	198,000	0.7	198,000	0.7	198,000	0.6	198,000	0.6
Regenerator	414,400	1.5	440,200	1.6	440,200	1.4	440,200	1.5
Total	27,871,100	100.0	26,887,800	100.0	31,725,000	100.0	30,153,900	100.0

(1) Heat of combustion, net char = heat of combustion of all gasifier char losses - heat of combustion of auxiliary fuel stream.

Table 5-26. SUMMARIZED HEAT BALANCE (Continued)

5.3.7   COMPARISON OF COMMERCIAL PLANT PROCESS DESIGN BASIS WITH PILOT PLANT
        OPERATING RESULTS

Table 5-27 presents in a concise form the end results of the pilot plant
experimental program - namely, a comparison of the pilot plant data base
with the commercial plant process design basis. Volume 10 of this report
gives details of the latter.

In the table, comparisons are made for the heat balances. The pilot plant
thermal inefficiencies, such as the sensible heat content of the outlet
streams minus that of the inlet streams, generally span the commercial
plant design values. The pilot plant thermal efficiencies never quite
matched the commercial plant design value, primarily because of the higher
heat losses associated with a pilot plant and because the nonprocess char
loss through the single-stage gasifier cyclone was not always compensated
for by use of regenerator auxiliary fuel.

In the table, comparisons also are made for 15 process design criteria
such as gasifier and regenerator temperatures, char retention time, meth-
ane yield, acceptor circulation rate, etc., as itemized. In all cate-
gories, the pilot plant operating ranges either spanned the commercial
plant design criteria or approached them very closely. No computerized
projections or extrapolations of the pilot plant process design data base
are needed.

5.3.8   CALCULATION OF SULFUR BALANCES

5.3.8.1 Gasifier

In work sponsored by the EPA[5], Consolidation Coal Co. studied the use
of $CaCO_3$ to desulfurize hot low-BTU fuel gas. Typical conditions were
$1600°F$ and 15 atm abs pressure. Sulfur was removed by the reaction,

$$CaCO_3 + H_2S = CaS + H_2O + CO_2 \qquad\qquad (5-49)$$
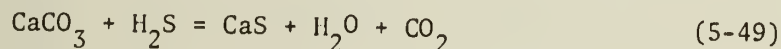
$$K_p = p_{H_2O}p_{CO_2}/p_{H_2S}$$

$$\ln K_p = 16.67 - .0018535T + .4809 \times 10^{-6}T^2 - 13977.2/T$$

$$p = \text{Partial pressure, atm}$$
$$T = °F$$

This work, done in a continuous system using fluidized bed reactors,
showed that equilibrium in the above reaction was approached closely.

Later, during some early runs in the Rapid City pilot plant, the gasifier
was isolated from the regenerator and its heat duty was supplied by partial
combustion with air. In these instances, the flow rates and sulfur con-
tents of all the solids streams could be measured. The H_2S content of gas
at the top of the fluidized bed then could be calculated by difference.
Data pertaining to these runs are shown in Tables 5-10 through 5-12, Sub-
section 5.3.6, and Tables 5-28 through 5-31 of this section. As

(5) Curran, G. P., et al, "Production of Clean Fuel Gas from Bituminous Coal."
    December, 1973, NTIS PB-232-695/AS. Work sponsored by EPA under Contract
    No. EHSD 71-15.

Heat Balance

	CO$_2$ Acceptor Process Commercial Design	Operating Range of the Rapid City Pilot Plant
In	100%	100%
Coal Feed, heat of combustion		
Out		
Heats of Combustion (% of total)		
Gasifier Streams		
Product Gas	84.2	73.7 - 81.2(e)
Net Char[1]	0	0.2 - 4.2(e)
NH$_3$ + H$_2$S	0.6	0.6 - 0.9
Regenerator Streams		
Flue Gas + H$_2$S + COS	2.6	2.3 - 5.2
Overhead Ash	0.5	0.5 - 0.7
Net Heats of Reaction		
MgCO$_3$ = MgO + CO$_2$	0	0 - 0.5
CaCO$_3$ = CaO + CO$_2$	0	0.4 - 2.1
CaO + S = CaS + O	0.4	< 0.1 - 0.3
Sensible Heats		
Outlet Streams - Inlet Streams	11.4	9.8 - 14.7
Heat Losses		
Gasifier	0.2	0.6 - 0.7
Regenerator	0.1	1.4 - 1.6
Total	100.0	
Process Design Criteria		
Bed Temperature, °F		
Gasifier	1520	1480 - 1528
Regenerator	1848	1835 - 1890
Mols Steam to Gasifier per 100 lb dry coal	5.38	5.14 - 6.42
Mols Air to Regenerator per 100 lb dry coal	7.35	7.35 - 9.57
Acceptor Circulation Rate, lb/hr/ft^3	2340	880 - 2680
% Fixed Carbon Gasified	60.1	50.1 - 61.0
Nominal Char Residence Time in Gasifier, hr[2]	3.3	2.8 - 5.1
Net Heat of Reaction per atom carbon gasified[3]	34,510	31,270 - 37,380
Mols CH$_4$ Produced per atom carbon gasified	0.196	0.198 - 0.244
Mols CH$_4$ in Raw Gas per mols CH$_4$ in SNG	0.365	.368 - .450
% Acceptor Duty met by Recarbonation Reaction	97.2	63.0 - 97.0
Acceptor Activity[4]	.21	0.09 - 0.20
ΔP$_{CO_2}$ Driving Force, atm[3]		
Bottom of Gasifier Bed	0.70	0.70 - 0.96
Top of Regenerator Bed	1.02	0.86 - 1.83
% Steam Conversion	68	49 - 63

[1] Heat of combustion, net char = heat of combustion of all gasifier char losses - heat of combustion of auxiliary fuel stream.

[2] Nominal char residence time = $\dfrac{\text{Gasifier Char Bed Inventory} \times \text{Fraction Char} \quad \text{(Lbs)}}{\Sigma(\text{Gasifier Char Exit Streams}) \qquad \text{(Lbs/hr)}}$

[3] Net heat of reaction = net heat of combustion (output - input, excepting acceptor) + heat of combustion of the CaS produced in the gasifier.

[4] Only for runs in which limestone acceptor was used.

[3] ΔP$_{CO_2}$ driving force = |P$_{CO_2}$(actual) - P$_{CO_2}$(equilibrium)|

[e] Excluding Run 45.

Table 5-27.   COMPARISON OF COMMERCIAL PLANT PROCESS DESIGN
BASIS WITH PILOT PLANT OPERATING RESULTS

see individual tables for details

Run	15B Preox. Velva Lignite	31-III Wyodak Subb.	31-II Sarpy Creek Subb.	39 Glenharold Lignite	45 Wyodak Subb.	46C Velva Lignite	47B Velva Lignite
Feedstock							
Gasifier Temperature, °F	1525	1480	1470	1490	1528	1490	1510
System Pressure, atm abs	11.1	11.1	11.1	11.0	11.0	13.9	11.0
Feed Rate, lb/hr	1120	1470	1530	2690	2140	2885	2720
Atoms/hr total sulfur fed	.224	.312	.364	.778	.701	.400	.557
K_p*	322.9	260.7	246.2	269.2	334.7	269.2	302.3
P_{CO_2}, atm	1.021	1.313	1.326	.6853	.8187	1.150	.7493
P_{H_2O}	1.140	2.162	2.072	2.602	2.870	3.676	2.367
Mols/hr H₂S Leaving Gasifier							
By Difference	.0670	.247	.237	.138	.194	.303	.178
By Model Reaction	.0650	.261	.264	.156	.142	.330	.129
100 x Model/difference	97	106	111	113	73	109	72

* Model reaction is: $CaCO_3 + H_2S \rightleftharpoons CaS + H_2O + CO_2$

$\ln K_p = 16.67 - .0018535T + .4809 \times 10^{-6} T^2 - 13977.2/T$

$T = °F$

Table 5-28. GASIFIER SULFUR BALANCE SUMMARY

see heat and material balance table for input data

Stream	Lb/hr	% S	Lb/hr S
In			
Coal	1120	.64	7.168
Out			
Cyclone Char	--		
Purged Char	138	.87	3.818
Quench Tower Char	166	2.30	1.201
		Total	5.019

S to gas by difference = 2.149 lb/hr = .0670 mols/hr.

Calculation of Outlet H_2S by Model Reaction

p_{CO_2}, atm 1.021

p_{H_2O} 1.140

K_p = 329.1

p_{H_2S} = 1.021 x 1.140/329.1 = .00354

mols/hr H_2S = .00354 x 75970/11.1/379 = .0650

Table 5-29.   DETAILS OF SULFUR BALANCE - RUN 15B

see heat and material balance table for input data

Stream	Lb/hr	% S	Lb/hr S
In			
Coal	1470	.68	9.996
Out			
Cyclone Char	153	.44	.673
Purged Char	136	.66	.898
Quench Tower Char	44	1.16	.510
		Total	2.081

S to gas by difference = 7.915 lb/hr = .247 mols/hr

Calculation of Outlet H_2S by Model Reaction

P_{CO_2}, atm 1.313

P_{H_2O} 2.162

K_p = 260.7

P_{H_2S} = 1.313 x 2.162/260.7 = .01089

mols/hr H_2S = .01089 x 99200/11.1/379 = .261

Table 5-30.   DETAILS OF SULFUR BALANCE - RUN 31-III
WYODAK

123

see heat and material balance table for input data

Stream	Lb/hr	% S	Lb/hr S
In			
Coal	1530	.75	11.475
Out			
Cyclone Char	185	.65	1.202
Purged Char	144	1.35	1.944
Quench Tower Char	52	1.39	.723
		Total	3.869

S to gas by difference = 7.606 lb/hr = .237 mols/hr

Calculation of Outlet H_2S by Model Reaction

P_{CO_2}, atm 1.326

P_{H_2O} 2.072

K_p = 246.2

P_{H_2S} = 1.326 x 2.072/246.2 = .01116

mols/hr H_2S = .01116 x 97700/11.1/379 = .264

Table 5-31. DETAILS OF SULFUR BALANCE - RUN 31-II
SARPY CREEK

124

summarized in Table 5-28 (Runs 15B, 31-I, and 31-II), close approach to equilibrium in Reaction 5-49 again was observed. In these runs, the source of $CaCO_3$ was the calcium in the ash of the low-rank Western coals which were used. These coals characteristically contain reactive calcium present in a large stoichiometric excess over their sulfur content.

Based on the above data, the process model uses equilibrium in Reaction 5-49 to dictate the sulfur content of the gas at the top of the gasifier bed.

Small amounts of COS definitely are present, but the assumption was made that all the sulfur is in the form of H_2S.

5.3.8.2   Regenerator

Earlier unpublished work by Consolidation Coal Co., done in 1962, indicated that equilibrium in the reaction,

$$CaS + H_2O = CaO + H_2S \qquad\qquad (5-50)$$
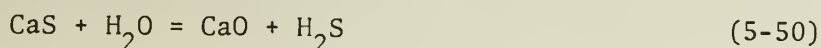
also was approached closely. During bench-scale development of the process in 1964-1968[3], COS, SO_2, and H_2S always were present in the regenerator overhead gas. To allow for COS, the model assumes equilibrium in the companion reaction to Reaction 5-50, which is:

$$CaS + CO_2 = CaO + COS \qquad\qquad (5-51)$$
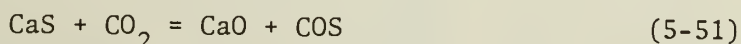
Equilibrium constants for Reactions 5-50 and 5-51 are, respectively:

$$1/K_p = \exp(17.5646 - .0092926T + 1.7716 \times 10^{-6}T^2 - 1070/T)$$

$$K_p = \exp(-20.7776 + .0106626T - 1.98418 \times 10^{-6}T^2 - 1611/T)$$

$$T = {}^oF$$

During the work described in Reference (3), in which the feedrates and sulfur contents of the fuel char and acceptor fed to the regenerator were measured, the total sulfur in the regenerator off-gas consistently was about 30 mol % of the total sulfur input; the remainder being CaS in the overhead char + ash.

5.3.8.3   Sequence of the Sulfur Balance

As the elemental and heat balances are being converged, the program calculates:

Gasifier

(1) H_2S in the outlet gas according to Reaction 5-50.

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(3)   Interim Report No. 3, Book 3, Phase II, <u>Bench-Scale Research on CSG Process - Operation of the Bench-Scale Continuous Gasification Unit</u>, January, 1970. Research and Development Report No. 16. National Technical Information Service PB-184720/AS.

(2) Sulfur flow rate in the char fed to the regenerator.
(3) Sulfur flow rate in the acceptor fed to the regenerator by difference between the coal sulfur feedrate and the sum of the measured gasifier cyclone solids sulfur rate, (1) and (2) above.

Regenerator

(4) Total sulfur fed to the regenerator is sum of (3), above plus known sulfur flow rates of the auxiliary fuel and makeup acceptor.
(5) H_2S and COS in the overhead gas according to Reactions 5-50 and 5-51.
(6) Total sulfur in the overhead gas as 30% of (4), above.
(7) *SO_2 in the overhead gas as the difference between (6) and (5), above.
(8) CaS in the overhead char plus ash as 70% of (4), above.

5.3.8.4   Notes on the Sulfur Content of Regenerator Outlet Solids

The model assumes that all of the coal ash and sulfur leave the top of the regenerator in the char + ash stream and therefore that the rejected spent acceptor contains no ash or sulfur.

Actually, a small amount of the coal ash does react with the recirculating acceptor and is removed with the reject acceptor stream. Also, a small amount of sulfur builds up in the recirculating acceptor to an equilibrium level of, typically, 0.15 wt% of the acceptor and is rejected with the spent acceptor stream. The only major exception to the small amounts of ash and sulfur rejected occurred in Run 39, as shown in Table 32.

From the standpoint of heat and material balances, the model assumption is equivalent to the actual situation, since all of the input ash and sulfur leave the top of the regenerator.

5.3.8.5   Test of Use of Reaction 5-49 in Model

Sulfur balances were calculated for Runs 39, 45, 46C, and 47B, during which the recirculating acceptor from the regenerator supplied all the gasifier heat duty. Heat and material balance data from the model are shown in Tables 5-20 and 5-22 through 5-24 of Subsection 5.3.6.

Sulfur balance data in which the gasifier H_2S is calculated by difference from the measured solids streams are shown in Tables 5-32 through 5-35. Results are summarized in Table 5-28. Closures for Runs 39 and 46C are substantially as good as for the earlier runs. The reasons for the poorer closures in Runs 45 and 47B are not apparent. These runs did not differ fundamentally from the companion runs.

---

*   If the SO_2 flow becomes negative (which has occurred only once) the program alters the 30/70 relationship to bring the SO_2 flow rate to zero or to a very small positive value.

see heat and material balance table for input data

Stream	MODEL			ACTUAL SOLIDS		
	Lb/hr	% S	Lb/hr S	Lb/hr	% S	Lb/hr S
In						
Coal	2690	.81	21.789	2690	.81	21.789
Auxiliary Fuel	180	1.75	3.152	180	1.75	3.152
Acceptor Makeup	~0	~0		~0	~0	
Total			24.941			24.941
Out						
Char from Regenerator	199	6.61	13.154	285	2.75	7.850
Atrited Acceptor	59	0	0	0	0	0
Reject Acceptor	336	0	0	306	1.92(2)	5.875
Subtotal	594			591		
Gasifier Cyclone Char	206	.57	1.174	206	.57	1.174
Regenerator Gas			5.676			5.676
Gasifier Gas			4.991			*
Total			24.995(1)			24.995

* S to gasifier gas by difference = 4.420 lb/hr

= .138 mols/hr H_2S

from model: .156 mols/hr H_2S

(1) Total does not match exactly the input total because of rounding.
(2) Reject acceptor sulfur content is high because of use of a high-sodium lignite. Sulfur is in form of sodium sulfide which had reacted with the acceptor.

Table 5-32. DETAILS OF SULFUR BALANCE - RUN 39

see heat and material balance table for input data

Stream	MODEL			ACTUAL SOLIDS		
	Lb/hr	% S	Lb/hr S	Lb/hr	% S	lb/hr S
In						
Coal	2140	.92	19.688	2140	.92	19.688
Auxiliary Fuel	304	.92	2.797	304	.92	2.797
Acceptor Makeup		~0			~0	
Total			22.485			22.485
Out						
Char from Regenerator	178	6.58	11.712	390(2)	2.54	9.906
Attrited Acceptor	61	0	0	0	0	
Reject Acceptor	245	0	0	93	.15	.140
Subtotal	484			483		
Gasifier Cyclone Char	162	.76	1.231	162	.76	1.231
Regenerator Gas			4.991			4.991
Gasifier Gas			4.568			*
Total			22.502(1)			22.502

* S to gasifier gas by difference = 6.234 lb/hr
$$= .194 \text{ mols/hr } H_2S$$
from model: $.142 \text{ mols/hr } H_2S$

(1) Total does not match exactly the input total because of rounding.
(2) The acceptor suffered size degradation unique in the history of operations. The resulting highly expanded fluidized bed caused most of the reject acceptor to be carried out with the overhead char and ash.

Table 5-33. DETAILS OF SULFUR BALANCE - RUN 45

see heat and material balance table for input data

Stream	MODEL			ACTUAL SOLIDS		
	Lb/hr	% S	Lb/hr S	Lb/hr	% S	Lb/hr S
In						
Coal	2885	.43	12.406	2885	.43	12.406
Auxiliary Fuel	101	.43	.434	101	.43	.434
Acceptor Makeup		~0			~0	
Total			12.840			12.840
Out						
Char from Regenerator	170	.19	.323	160	.56	.896
Attrited Acceptor	23	0	0	0	0	0
Reject Acceptor	130	0	0	184	.15	.276
Subtotal	323			344		
Gasifier Cyclone Char	143	.43	.615	143	.43	.615
Regenerator Gas			1.294			1.294
Gasifier Gas			10.574			*
Total			12.806(1)			12.806

$*$ S to gasifier gas by difference = 9.725 lb/hr
 = .303 mols/hr H_2S
from model: .330 mols/hr H_2S

(1) Total does not match exactly the input total because of rounding.

Table 5-34. DETAILS OF SULFUR BALANCE - RUN 46C

see heat and material balance table for input data

Stream	MODEL			ACTUAL SOLIDS		
	Lb/hr	% S	Lb/hr S	Lb/hr	% S	Lb/hr S
In						
Coal	2720	.52	14.144	2720	.52	14.144
Auxiliary Fuel	153	.52	.796	153	.52	.796
Acceptor Makeup	268	1.084	2.905	268	1.084	2.905
Total			17.845			17.845
Out						
Char from Regenerator	163	5.54	9.030	185	3.83	7.086
Attrited Acceptor	39	0	0	0	0	0
Reject Acceptor	222	0	0	259	.15	.389
Subtotal	424			444		
Gasifier Cyclone Char	171	.44	.752	171	.44	.752
Regenerator Gas			3.891			3.891
Gasifier Gas			4.144			*
Total			17.817(1)			17.817

* S to gasifier gas by difference = 5.699 lb/hr
= .178 mols/hr H_2S
from model: .129 mols/hr H_2S

(1) Total does not match exactly the input total because of rounding.

Table 5-35. DETAILS OF SULFUR BALANCE - RUN 47B

5.3.9   PARTICLE PROPERTIES

Routine analysis of solids samples were performed in the pilot plant lab-
oratory as described in Section 3, Book 1. These data were used primarily
to monitor the daily operating conditions of the plant. Specific samples
collected during selected balance periods were chosen for more detailed and
comprehensive analysis. This work was performed at the Library laboratory
to determine the compositions of the specific solids necessary for the cal-
culation of heat and material balances. In general, all samples were sepa-
rated into two or more size fractions and specified analyses performed on
each size fraction. The final compositions were arrived at by weight aver-
aging the mean composition of each size fraction. By comparing the
compositions of the individual size fractions, the observer can more
easily detect spurious values which may be the result of analytical
error, sampling technique, or contamination. In cases where atypical
values were observed, the sample was either rejected or the particular
analysis was repeated. As a general rule, all carbon and hydrogen values
represent the average of duplicate determinations. Specific details
of other sample work-up performed at Library are described in Section 5.7.
Standard analytical methods employed by the Library analytical laboratory
are listed in Table 3.1 of Volume 12, Book 1.

5.3.9.1   Feedstocks

5.3.9.1.1 Gasifier Feedstocks

Tables 13-1 through 13-3, Appendices Subsection 13.4 of Book 4, list the
ultimate and ash elemental compositions and the size distributions of
the gasifier feedstocks that were used in the runs for which heat and
material balances have been calculated.

5.3.9.1.2 Regenerator Auxiliary Fuel

Regenerator auxiliary fuel compositions are listed in Tables 13-14
through 13-16, Appendices Subsection 13.4 of Book 4. Husky char was
used as auxiliary fuel for the regenerator in Runs 26 to 39. Velva
lignite fed from tote bins was used for Run 40. This was the first run
in which a coal had been used as auxiliary fuel.

5.3.9.1.3 Acceptor Feedstocks

Typical compositions of the acceptor feedstocks are listed in Tables
13-17 and 13-18, Appendices Subsection 13.4 of Book 4. Acceptor com-
positions for each run are not listed because the natural stone was
generally quite uniform in composition. Analyses were performed only
as a check when new shipments were received.

5.3.9.2   Process Solids

Process solids consist of gasifier bed material, recarbonated acceptor
and calcined acceptor. Of primary importance are the recarbonated ac-
ceptor and the gasifier bed solids.

131

5.3.9.2.1   Recarbonated Acceptor

The recarbonated acceptor samples were used to determine the acceptor
activity and were processed as described in Section 5.7. Tables 13-19
through 13-28, Appendices Subsection 13.4 of Book 4 list the recarbonated
acceptor activity, particle density and size distribution for the heat
and material balance runs.

5.3.9.2.2   Gasifier Bed Solids

The gasifier bed material samples were separated into the three components
(char, acceptor, and intermediate fines) by the methods described in
Section 5.7. Tables 13-29 through 13-38, Appendices 13.4 of Book 4, list
the breakdown of the three components in the gasifier bed. The compositions
of the char fraction are listed in Tables 13-39 through 13-51, Appendices
Subsection 13.4. It should be noted that these compositions are of the
char component only. The 35 x 65 mesh fraction was not analyzed because
of the inability to separate the char from the acceptor and intermediate
fines in this size range.

5.3.9.3   Effluent Solids

Gasifier quench tower solids compositions are listed in Tables 13-52
through 13-63, Appendices Subsection 13.4. The gasifier external cyclone
solids compositions are listed in Tables 13-64 through 13-73, Appendices
Subsection 13.4.

The regenerator overhead solids compositions are listed in Tables 13-74
through 13-82. Purged char and acceptor compositions are listed in
Tables 13-83 through 13-92. (See Appendices Subsection 13.4.)

5.3.10   DEPOSITS

5.3.10.1   Gasifier Deposits

During many runs throughout the pilot plant program, gasifier deposits
were formed. The deposits can be categorized as:

(1)   Deposits caused by equipment geometry.
(2)   Deposits formed due to process upsets.
(3)   Process derived deposits.

5.3.10.2   Equipment Geometry and Process Upset Deposits

Figure 5-17 shows the locations of the most common deposits caused by
equipment geometry and process upsets. The boot wall deposits are typical
of geometry-caused deposits. Dead-burned dolomite and active acceptor
collect in the area behind the gas distributor bubble caps and between
the distributor ring and the refractory wall. In this area, which is
in effect in the shadow of the distributor ring, the solids are not
fluidized. At the operating conditions of pressure and temperature,
which are maintained in the CO_2 acceptor process reactor, nonfluidized
acceptor solids will eventually agglomerate due to the formation of
crystallite bridges between touching particles.
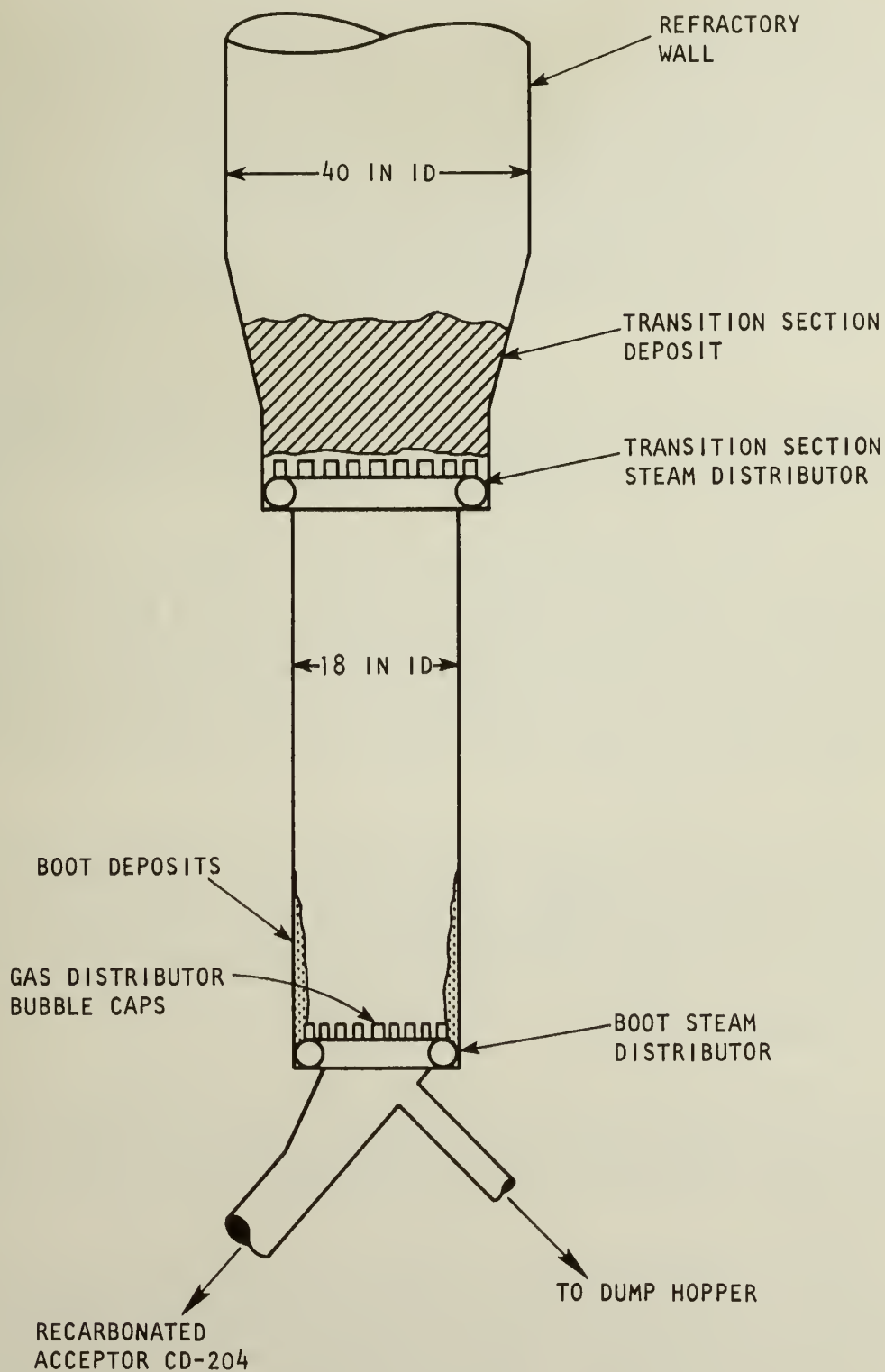
Figure 5-17. LOCATION OF GASIFIER DEPOSITS

133

During most runs the boot deposits did not cause any operating problems. The deposits generally acted as a funnel directing the recarbonated acceptor into the CD-204 standleg. However, efforts were made to eliminate the deposits, since the possibility existed that a portion of the deposit might break away from the wall and plug the recarbonated acceptor standleg; and during some runs the deposits increased the gas inlet velocity to the boot with respect to the velocity near the top of the boot enough to interfere with the char-acceptor interface stability. Total elimination of the boot deposits was not routinely achieved during the pilot plan operations. However, progress was made in minimizing the size of the deposits through modification of the boot gas distributor design. Further improvements in the distributor design appear to be easily achievable.

The most common gasifier deposit caused by process upset is shown in the transition section of the reactor. Any time the char-acceptor interface level rose into the transition section, due to the loss of acceptor transfer from the boot, instrumentation malfunctions, or power failures, this type of deposit was likely to form.

In the transition section the gas velocity is normally insufficient to fluidize char-stripped acceptor. An interface level in the transition section will result in a large amount of nonfluidized acceptor. which with time will agglomerate as crystallite bridges form between particles. If during an upset the temperature in the transition section drops below $1300^\circ F$, the steam partial pressure in the reactor must be dropped below 6 atm; otherwise, $Ca(OH)_2$ will form. Phase changes in the $CaCO_3$-CaO-$Ca(OH)_2$ system will then produce liquid melts which will instantly cause acceptor agglomeration.

As long as interface levels were maintained in the gasifier boot, no transition section deposits formed. In addition, a special operating procedure which is presented in Subsection 13.2.1 , Book 4, was developed which allowed routine recovery of the pilot plant operations when interface levels rose into the transition section. The special interface recovery procedure was a successful means of preventing transition section deposits.

5.3.10.3 Process-Derived Deposits

Process-derived deposits in the gasifier are related to the sodium present in the mineral matter associated with lignite. Since the vast lignite reserves in the Northern Great Plains vary from about 1 to 16% Na_2O in ash (sulfur free basis), it is clear that sodium content must be a consideration in the selection of a raw material reserve for lignite gasification.

Two types of gasifier deposits are encountered when using lignites of moderate to high sodium content. The first type occurs during plant start-up when air is injected into the gasifier to aid in maintaining the char bed temperature. Fused ash deposits form in front of the transition section distributor, as typified by Runs 32, 34, and 35 with Glenharold lignite (8% Na_2O in ash). The deposits resembled fingers or tubes 3 to 6 inches long and 1 to 2 inches in outside diameter, extending both horizontally and vertically from the distributor bubble caps. They contain 10-15% Na_2O and 41-46% SiO_2.

134

The formation of the deposits apparently results from localized hot spots at the air distributor. By modifying the start-up procedure to totally avoid the use of air in the gasifier while feeding raw coal, the deposit formations were totally eliminated and so do not constitute a problem to the CO_2 Acceptor Process. However, the formation of such deposits has significant implications regarding the practicality of using moderate to high sodium content lignites in other fluidized bed gasification processes which utilize oxygen injection into a gasifier char bed. During Run 35, the oxygen partial pressure at the transition section gas distributor never exceeded 0.5 atmospheres when high sodium Glenharold lignite was fed to the reactor. Even at this low partial pressure, slag deposits formed. Therefore, it is doubtful that oxygen injection processes will be operable.

The second type of sodium-caused deposit formed during Run 36. As a result of reaction between the acceptor and char ash, some sodium is transferred to the acceptor particles. In Run 36 the sodium level in the acceptor reached 2.5 wt % Na_2O. This caused a sudden total agglomeration of all the acceptor in the gasifier boot. Laboratory tests indicated that the problem could be avoided by maintaining a 1500^OF boot temperature and by operating at a slightly lower boot steam partial pressure (10 atm rather than 11.6). During Run 39 a conservative approach was taken, rather than operating at 10 atm steam partial pressure the partial pressure was maintained at about 9 atm. The sodium buildup in the acceptor stabilized at about 0.6 wt % Na_2O and no agglomeration occurred. The run clearly demonstrated that lignites containing 8.0 wt % Na_2O in the sulfur-free ash can be utilized by the CO_2 acceptor process. Thus, the process can utilize the majority of the lignites in the Northern Great Plains region of the United States.

5.3.10.4 Regenerator Vessel Deposits

During the early pilot plant operations, runs prior to Run 16, the acceptor inventory was established by filling the regenerator with raw dolomite. The use of fresh acceptor for the initial acceptor inventory resulted in the formation of massive wall scale deposits in the regenerator. The majority of the wall scales, which at times were several inches thick near the bottom of the vessel, were apparently formed when the acceptor inventory was first calcined as the regenerator was heated to the operating temperature of 1850^OF.

When raw acceptor is first calcined, a soft, easily attrited material is formed. However, as the acceptor experiences several calcination-recarbonation cycles during passage through the regenerator and gasifier reactors, a hard, attrition resistant material is formed. The early regenerator calcinations produced a regenerator inventory which was totally composed of soft acceptor particles. This resulted in the production of large quantities of reactive and sticky acceptor fines which formed the wall deposits. The stickiness of the acceptor fines was apparently caused by the transient liquid which is known to exist for the $CaS-CaSO_4$ system. Because of the large surface area of the fines, even minute amounts of liquid melts would cause fines agglomeration. The fines also hindered the calcined acceptor flow, due to the formation of fines-induced solids plugs in the CD-206 standleg.

The regenerator deposits and standleg plugs were overcome by modifying the start-up procedure to eliminate the initial fresh acceptor inventory. The new start-up procedure incorporated the use of dead-burned dolomite for the initial regenerator inventory. Dead-burned dolomite is a material which has been fired to 3400°F. This treatment calcines the dolomite and destroys the internal pore structure, producing a rugged material which is inert to the reactions of the CO_2 acceptor process. Thus, once the regenerator is filled with dead-burned dolomite, the reactor can be heated rapidly to the 1850°F operating temperature. The dead-burned dolomite inventory is then gradually replaced by the make-up of fresh acceptor to the regenerator and the withdrawal of spent acceptor from the regenerator. When the dead-burned dolomite inventory is changed-out, the acceptor inventory is made up of a complete spectrum of particles with differing ages and hardnesses. Since at any instant the fresh acceptor make-up represents only a small fraction of the regenerator bed material, few fines are present in the reactor. The system is tolerant of these fines. The fines are eventually stripped from the inventory and are carried out of the reactor with the regenerator flue gases.

Figure 5-18 shows typical regenerator deposit buildups for Run 16 and beyond. Between Runs 16 and 41, thin scales (which were high in sulfur content and were composed primarily of acceptor fines) normally formed on the reactor walls. These scales adhered strongly to the reactor walls and did not cause any process problems. The scale thickness was apparently limited by the scrubbing action of the fluidized acceptor bed.

A thicker deposit formed along the lower walls of the reactor. The material nearest the reactor wall was normally loose dead-burned dolomite. The material on top of the dead-burned dolomite was a mixture of acceptor and fused char ash. Apparently the distributor ring created a zone in which bed material solids became defluidized. The char particles trapped in the area burned at high enough temperatures to cause some ash fusion. The deposit formed a stable geometry and never interfered with the reactor operation.

After Run 41, the regenerator was lined with refractory brick to reduce the reactor internal diameter so that the commercial operating practice of using air alone to fluidize the calcining acceptor could be demonstrated. The brick lining covered the air ring distributor eliminating the stagnant area. This reactor geometry change totally eliminated the bottom end deposits. Thin wall scales still formed. However, these scales were thinner (normally not exceeding 1/8-inch in thickness) than the scales for the nonbrick lined regenerator. Presumably, the higher inlet fluidizing gas velocity (which was 3.5 to 4.0 ft/sec for the brick-lined vessel, versus the 2.5-3.0 ft/sec for the nonlined vessel) was responsible for the thinner scale thickness.

For both the brick-lined and nonlined vessel operations, deposits formed in the inlet cone section just ahead of the air ring distributor. The deposits were composed of agglomerated dead-burned dolomite. The deposit formed a steeper inlet cone to the reactor. Since the deposit formed a stable geometry, it was often left in the reactor after a run. No deposit would have formed had the inlet refractory cone been designed with a more acute included angle.
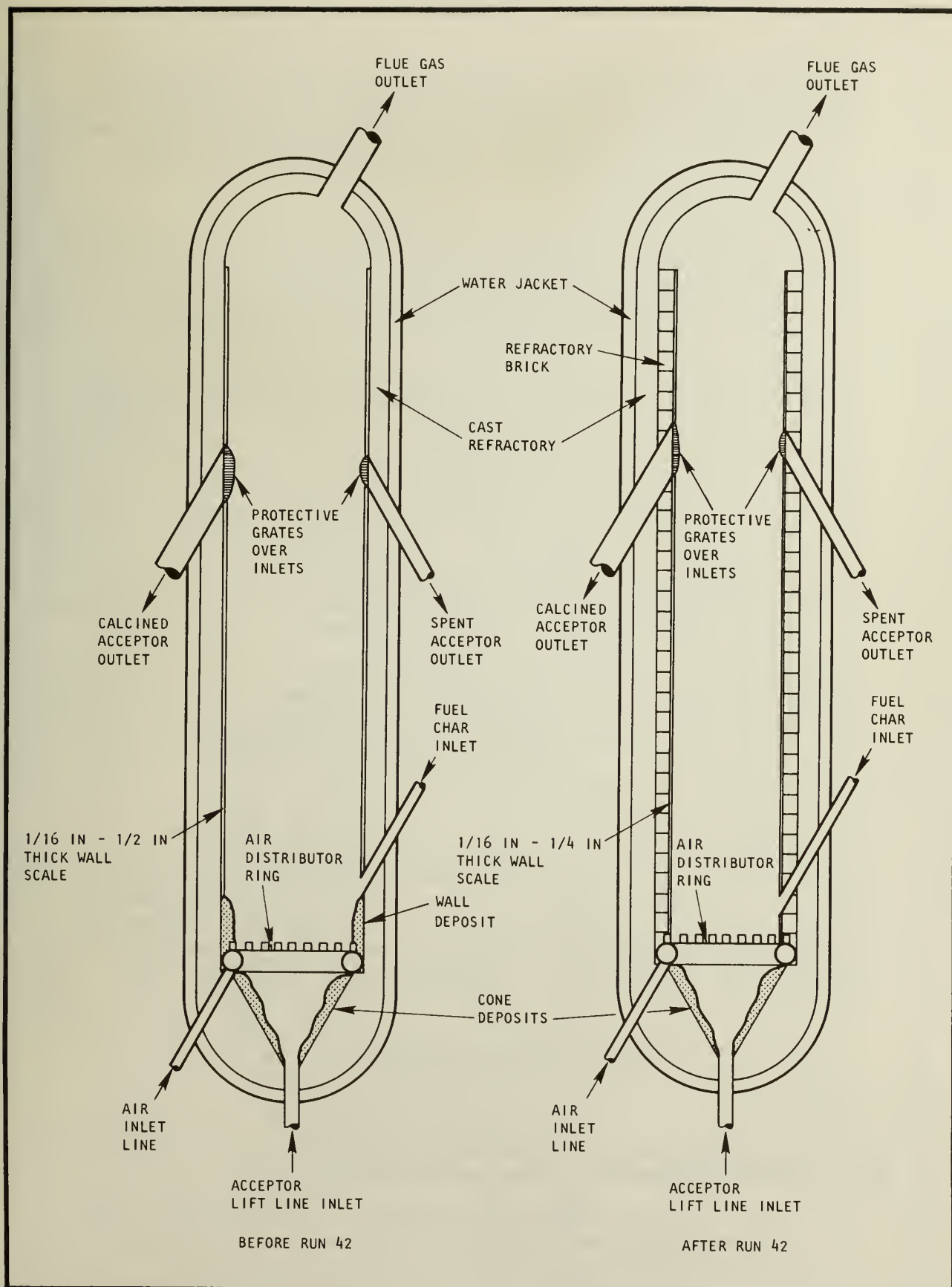
Figure 5-18. TYPICAL REGENERATOR DEPOSITS

137

Based on the experience with sodium-related deposits in the gasifier, similar deposits might be anticipated in the region of air combustion of the regenerator. The available data show that sodium deposits accumulate on the acceptor surfaces rather than on the regenerator internals.

5.3.10.5 Flue Gas Outlet Deposits

During several runs (but not all runs) when Velva lignite or Glenharold lignite were used as feedstocks, deposits composed of ash and acceptor fines formed in the gooseneck section which connects the regenerator flue gas nozzle with the water-cooled flue gas line to the ash cyclones. Figure 5-19 shows the location and extent of the Run 46C deposit.

Although the deposits restricted the gas exit pipe opening to approximaterly 1/3 of the original cross-sectional area, the deposits did not noticeably interfere with the pilot plant operation. Piping geometry may play a key roll in the formation of the deposits. The deposits have been almost totally (98%) confined to the gooseneck portion of the flue gas line. In the gooseneck the gas flow undergoes a 210-degree directional flow change. Essentially, no deposit forms in the straight lines which lead to and from the gooseneck section. A more important factor which may affect the deposit formation is the local temperature condition in the gooseneck section. The gooseneck is the first section of flue gas line which is water jacketed. The flue gases may cool enough to allow some recarbonation of acceptor fines which could lead to the formation of the deposits.

The gooseneck deposits are not expected to be a problem in commercial plants, since heat is not removed from the flue gases until the ash and attrited acceptor fines have been removed. The removal of the fines at the reactor exit conditions should eliminate the formation of deposits.

5.3.10.6 Calcined Acceptor Standleg Deposits

Scale deposits, composed mainly of recarbonated acceptor fines, formed in the calcined acceptor standleg during several runs. The apparent cause of the deposits was the recarbonation of acceptor fines at the walls of the standleg. The line scales were eliminated by installing several nitrogen purges near the inlet to the standleg. The nitrogen purges stripped the CO_2 containing flue gases which accompanied the acceptor into the standleg. By eliminating the interstitial CO_2, recarbonation of fines in the standleg could not take place.

5.4   REGENERATOR OPERATION

5.4.1   CALCINATION

Information defining the effectiveness of the regenerator for acceptor calcination is contained in the following subsections:

(1) Gasification Heat and Material Balances, Subsection 5.3.6. This section contains the composition of the acceptor entering and leaving the regenerator.
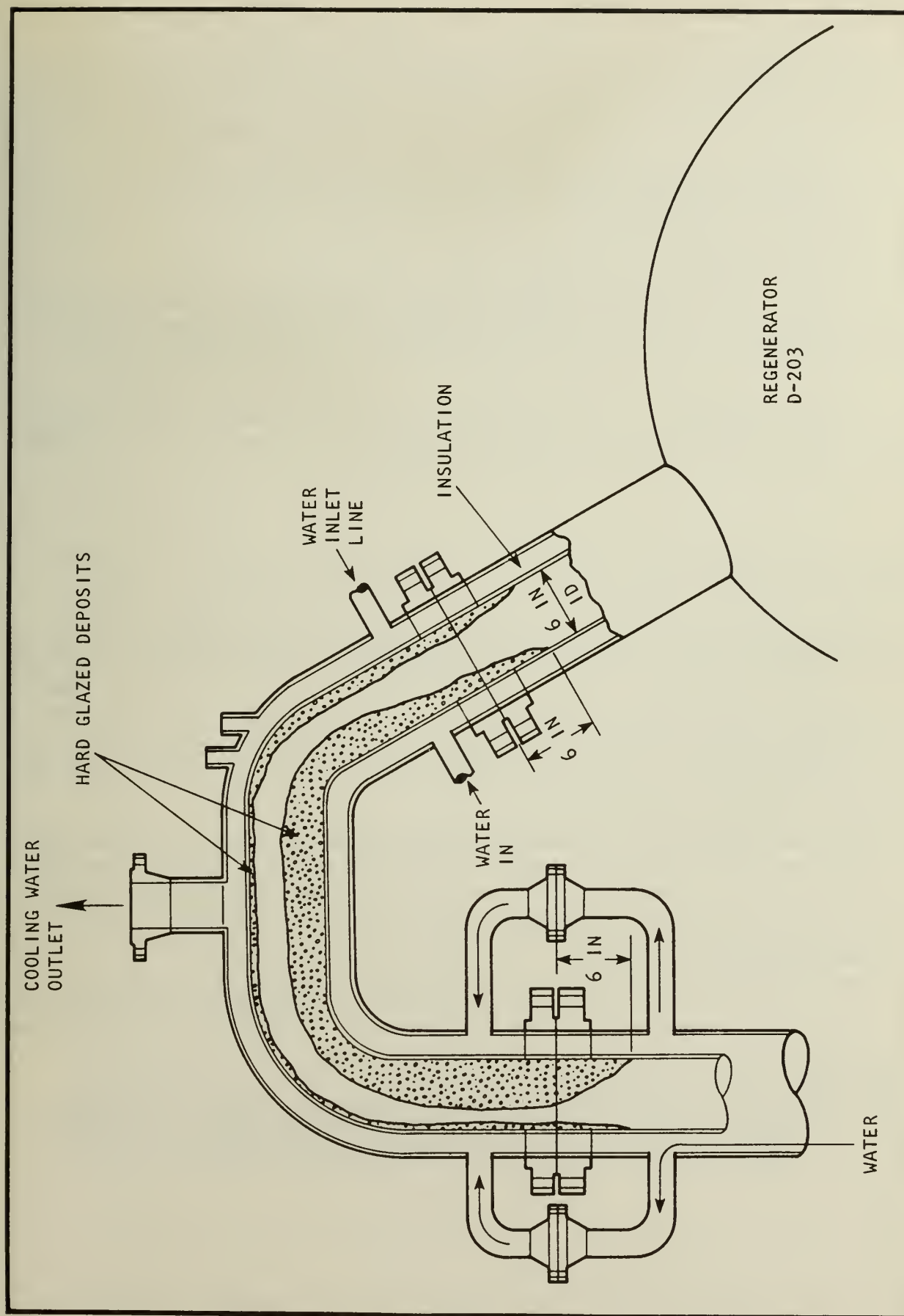
Figure 5-19. REGENERATOR FLUE GAS NOZZLE AND GOOSENECK SHUTDOWN 46C

139

(2) Acceptor Peformance, Subsection 5.5. This section provides infor-
     mation on the impact of regenerator variables on acceptor performance.

No specific study of acceptor regenerator kinetics was carried out at
Rapid City. Under the conditions employed (1850°F and 15-60 minutes
residence time), acceptor withdrawn from the regenerator was always
completely calcined. This is consistent with the results of prior
bench-scale studies[3].

5.4.2   CHAR COMBUSTION

Char is fed as fuel to the regenerator to provide heat for the endothermic
calcination of the recarbonated acceptor. Most of the regenerator fuel
requirements are met by using gasifier char. A slipstream of a mixture
of partially gasified char and acceptor is removed from the gasifier
char bed through standleg, CO-202, and then pneumatically conveyed to
the regenerator in the char lift line, CO-204. The char-acceptor mixture
is then combined in the regenerator with acceptor entering the regenerator
by way of the acceptor lift line, CD-208.

The regenerator bed of acceptor is fluidized by air, and in the early
runs, by a combination of air and recycled regenerator flue gas. Gas
enters the regenerator from the acceptor life line, CD-208, and through
the distributor ring located at the bottom of the regenerator. Under
normal process conditions, only air is sent to the distributor ring. In
the lift line, recycle flue gas was used before Run 42. After Run 40B,
the acceptor lift line was lined with refractory. The refractory lining
allowed the use of 100 percent air as lift gas. High temperatures resulting
from the combustion of char that might enter the line with acceptor from
the gasifier boot would be withstood by the refractory. The possibility
of this happening before the lift line was lined with refractory had
prevented the earlier use of air for acceptor lift gas. One-hundred precent
air was used for the first time in Run 42. In all subsequent runs, air
was used as acceptor lift gas.

The air admitted to the regenerator also supplies the oxygen for combustion
of the char. Normally, 75,000 to 85,000 SCFH of air is needed. The total
gas flow in the acceptor lift line is usually about 60,000 SCFH, so when
this is 100-percent air, most of the air required for combustion enters
the regenerator from the lift line. The air flow to the distributor ring
is then about 20,000 SCFH.

The temperature in the regenerator fluid bed is controlled at about 1850°F.
This high temperature is needed to provide the driving force for calcination

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(3) "Phase II, Bench-Scale Research on CSG Process-Operation of the Bench
    Scale Continuous Gasification Unit" OCR R & D Report No. 16, Interim
    Report No. 3, Book 3, January 1970, HTS PB-184 720/AS.

of the acceptor. The fluidized bed in the regenerator provides good mixing of the char and acceptor. As a result, the heat released by char burning is dispersed throughout the bed so that the temperature gradient between the top and bottom of the bed is usually no more than than about 30°F. The heat released from char burning is on the order of 7 to 8 million Btu/hr.

The regenerator temperature is controlled by adjusting the air flow to the regenerator. Since the total gas flow in the lift line must be set at a certain level (60,000 SCFH) in order to insure transport of the acceptor solids up the lift line, air flow changes are made in the distributor ring air flow. High temperatures are brought down by decreasing ring air flow so that less char combustion takes place. Likewise, when regenerator temperatures are low, air flow is increased to the ring so that more combustion takes place and the bed temperature increases.

High carbon burn-out levels are achieved in the regenerator. Nearly all the char feed to the regenerator is burned to a fine ash which is elutriated out of the regenerator bed. The small amount of carbon present in the ash normally represents less than 1% of the total carbon fed to the gasifier.

The regenerator is operated with a reducing atmosphere in order to prevent transient liquid-derived deposits. The carbon monoxide concentration is held in the range of 1 to 5%. This small percentage of CO has been shown in bench-scale work to prevent deposit formation. In the pilot plant, no problems with regenerator deposits occurred while the regenerator was operating under reducing conditions.

While a small percentage of CO in the regenerator exit gas is desirable for the purpose of preventing deposits, high CO levels are undesirable in both the pilot plant and in a commercial plant. During startup and throughout the early pilot plant runs, regenerator overhead gas was frequently recycled back to the regenerator. If the gas contains a large percentage of CO, rapid combustion of this gas will take place at the regenerator inlet. Localized high temperatures could result and cause the char ash to fuse.

The CO concentration in the regenerator is controlled by regulating the rate of char transfer from the gasifier. High CO concentrations are lowered by reducing char transfer from the gasifier, and low CO concentrations are brought up by increasing char transfer.

During startup, the regenerator is initially heated up by recycling hot gas through the vessel. The recycle gas is heated by natural gas-fired furnaces. When the regenerator reaches 1000°F, char transfer from the gasifier is established. Char combustion continues the heating of the regenerator to the process temperature of about 1850°F.

A minimum of 800°F is required in the regenerator before char combustion is attempted. This requirement insures that the char fed to the regenerator will burn immediately.

5.4.3   USE OF AUXILIARY FUEL

Auxiliary fuel is fuel fed to the regenerator in addition to the char withdrawn from the gasifier. Natural gas was initially used as auxiliary fuel, but it was later replaced by a solid fuel system.

After Run 25, a solid feed system consisting of lockhoppers and a rotary feeder (see Figure 5-7) was installed on the char lift line, CO-204. This system fed solid fuel into the char lift line, to be transported to the regenerator.

Char was used as auxiliary fuel for the first several runs. In Run 40A dried lignite, and in Run 41A subbituminous coal, were used as auxiliary fuels for the first time. Lignite or subbituminous coal was used in all subsequent runs.

The auxiliary fuel system provided the process with another degree of freedom and made plant operation more flexible. The use of auxiliary fuel served several purposes, which included:

(1)   Auxiliary fuel aids in the startup of both the regenerator and gasifier.
(2)   Auxiliary fuel provides a reliable source of fuel for the regenerator during char transfer upsets.
(3)   The fixed carbon burn-off level in the gasifier can be adjusted without any effect on the regenerator.
(4)   The commercial practice of re-injecting gasifier overhead char fines back into the system can be simulated.

Auxiliary fuel fed to the regenerator during startup provides some of the regenerator fuel requirements that would otherwise be char from the gasifier. Char can then be withdrawn from the gasifier at a lower rate. The lower char withdrawal rates allow more gasification of the char particles, thereby lowering the char particle density. Acceptor showering through the gasifier char bed is facilitated by a less dense char bed, so the acceptor circulation rate can be maintained at a reasonable level. This aids gasifier startup, since the circulating acceptor can now take on more of the gasifier heat duty.

Auxiliary fuel also allows char transfer upsets to be handled without affecting regenerator operation. When char transfer from the gasifier is lost, the auxiliary fuel feed rate is increased to supply all of the regenerator fuel requirements. This keeps the regenerator up to operating temperature and allows acceptor calcination to continue.

The total fuel feed to the regenerator can be maintained by increasing the auxiliary fuel feed rate as char transfer from the gasifier is lowered. Thus, regenerator operation is not affected by adjustments made in gasifier operation.

The use of auxiliary fuel simulates the commercial operating practice of returning gasifier overhead char fines back to the system. In the pilot plant, the gasifier overhead fines (and the quench tower solids) are discarded. In a commercial coal gasification plant, however, all of the coal feed is utilized completely in order to maximize efficiency. Unreacted fines that are entrained out of the gasifier would be separated from the gas stream through the use of cylones and fed back to the regenerator to be used for fuel. The feed system for the fines in the commercial plant would be similar to the pilot plant auxiliary fuel feed system.

Usually, the auxiliary fuel feed rate was set to equal the rate at which carbon contained in the gasifier char fines was leaving the gasifier overhead. This simulated commercial practice more fully, since in a commercial plant the two streams are the same. The two rates could usually be maintained approximately equal, as long as an operational upset did not occur that necessitated a change in the auxiliary fuel feed rate or caused a change in the gasifier overhead solids rate.

Auxiliary fuel is brought onstream after char transfer to the regenerator has been established. The feeder is set at a low rate (approximately 100 to 200 lb/hr) and remains at this rate unless conditions require a change. At this feed rate, the auxiliary fuel feed rate will be about equal to the gasifier overhead solids rate when the targeted process conditions are reached.

In order to maintain smooth flow of char out of the lockhoppers and into the char transfer line, a purge is put to the lockhoppers (see Figure 5-7.) The differential pressure, dP-2098, between the lower lockhopper and the auxiliary fuel inlet line to the char transfer lift line is used to control the purge, so that the lockhopper pressure is kept higher than that downstream at the inlet line.

A thermocouple, TE-2408, in the auxiliary fuel line indicates whether auxiliary fuel is still flowing in the line. Auxiliary fuel is cooler than the char in the lift line, so it causes a drop in temperature when it enters the lift line. Therefore, whenever auxiliary fuel flow stops a temperature rise is noted on the control room chart recorder. Operators then take appropriate action to re-establish the auxiliary fuel feed.

5.4.4   OXIDIZING OPERATION

The original concept of regenerator operation was to operate at reducing conditions with 1-5 mol % CO in the regenerator flue gas. This was considered necessary to avoid deposit formation which was experienced during operation of the bench-scale gasification unit. About midway in the operating program of the pilot plant, and after technical feasibility had been demonstrated, the decision was made to determine if the bench-scale results were totally applicable to the pilot plant regenerator. The incentive to operate the regenerator under oxidizing conditions came from the increased process thermal efficiency which would be obtained by converting all of the carbon in the regenerator to CO_2. This would also eliminate the need for CO oxidizers in the commercial design flue gas system.

5.4.4.1   Background

Bench-scale unit operation revealed that the presence of sulfur in the regenerator when operated at stoichiometric combustion conditions (less than 1% CO in the outlet gas) almost always resulted in the formation of large deposits. Studies revealed that the mechanism for the formation of these deposits was the formation of a low melting transient liquid composed of CaS and $CaSO_4$, which glued the attrited acceptor fines and acceptor particles together. It was concluded that the source of this low melting transient liquid was CaS from both the fuel char and the incoming acceptor. At stoichiometric or oxidizing conditions, the CaS is oxidized to $CaSO_4$ by reactions:

$$1/4 \ CaS + CO_2 = 1/4 \ CaSO_4 + CO \qquad\qquad (5-52)$$

$$1/4 \ CaS + 1/2 \ O_2 = 1/4 \ CaSO_4 \qquad\qquad (5-53)$$
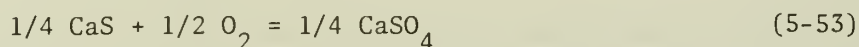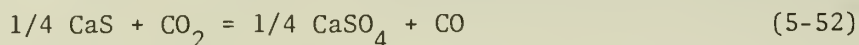
The transient liquid forms when $CaSO_4$ and CaS are present simultaneously. Therefore, the key to prevention of transient liquid formation was Reaction 5-52; to increase the CO content of the regenerator gas beyond the equilibrium level. This prevented the formation of $CaSO_4$ via either of the two reactions, which in turn eliminated the deposits. For this reason, no attempt to operate the regenerator at oxidizing conditions was made during the early stages of the pilot plant operating program.

Although several early pilot plant runs produced the transient liquid-type deposits in the regenerator, these deposits were formed during plant upset conditions when oxygen breakthrough occurred in the regenerator. At this time the use of dead-burned dolomite as a start-up material had not yet been instituted. Therefore, the initial regenerator inventory was entirely fresh acceptor which attrits more easily than aged acceptor and thus produces more fines. Bench-scale experience indicated that the transient liquid formed uniformly throughout the acceptor particle. Because small particles provide more surface area, more liquid is available for contact with other particles, which greatly enhances deposit formation.

After the successful demonstration of the CO_2 acceptor process feasibility was achieved in Run 33B, the possibility of being able to operate the pilot plant regenerator under oxidizing conditions became very conceivable. There was a good probability that the particle size alone of the pilot plant acceptor would allow regenerator operation under oxidizing conditions. The acceptor used in the bench-scale operation was nominally 16 x 28 Tyler mesh, while the pilot plant acceptor was nominally 8 x 12 Tyler mesh. The larger acceptor particles provide less surface area as well as a larger mass and momentum. This, coupled with a fluidizing velocity of two to three times that of the bench-scale regenerator, should all tend to decrease the potential for deposit formation.

5.4.4.2   Results

Run 43 was the first attempt to operate the regenerator at oxidizing conditions. The plan was to execute a normal startup, operate the regenerator for a period of time under the normal reducing conditions, and then phase

into a neutral condition (i.e., 0-1% CO in the regenerator flue gas) for a period of time and finally increase the air flow until the regenerator flue gas contained approximately 1% oxygen. This objective was not achieved in either Run 43A or 43B because of premature shutdowns. Because time did not allow another run to be devoted to demonstrating oxidizing operation of the regenerator, the objective was added to Run 45. All objectives for Run 45 were achieved. The regenerator was operated at neutral conditions for 8 hours, then at oxidizing conditions for the last 30 hours prior to voluntary termination of the run. No indications of any operational problems were evident during either the neutral or oxidizing periods of the run. After the run an inspection revealed that the regenerator was essentially free of deposits. A thin, 1/4-inch thick wall scale covered the upper two-thirds of the vessel. The thermocouple probes were covered with the same type of scale material that had been witnessed after many previous runs. Some of this material had lodged in the metal grate over the inlet of the calcined acceptor standleg. The formation of this type of deposit would be insignificant in a commercial scale regenerator, because the total mass of the deposits formed would be proportional to the number of thermocouples installed and not to the size of the regenerator. It is also quite conceivable that deposit formation on thermowells could be eliminated through the proper selection of materials. Since the deposits appeared to form preferentially on the colder metal surfaces of the thermowells, the use of an insulating-type material rather than metal may be advantageous in that the rate of heat transfer from the hot and to the cold end would be reduced.

Bench-scale experience indicated that a massive deposit should have formed in the regenerator under the conditions imposed during Run 45. The absence of any significant deposit formations indicate strongly that oxidizing operation should be considered in any future plant.

5.5 ACCEPTOR ACTIVITY

Acceptor activity is a measure of the ability of a given material to absorb or react with carbon dioxide (CO_2) gas. This is a very important parameter in the operation of a CO_2 acceptor gasification plant, as it is the reaction between CO_2 and calcium oxide (CaO) that (1) supplies a large percentage of the heat required for gasification and (2) eliminates the need for a water-gas shift conversion unit, since the removal of CO_2 causes increased hydrogen (H_2) production.

Traditionally, the acceptor activity has been defined by the following equation:

$$R = \frac{W}{C \times F_2} \qquad (5-54)$$

where W is the weight of CO_2 released from the acceptor upon calcination, C is the calcined sample weight and F_2 is a gravimetric factor specific to each acceptor (See Section 5.7 of this report for a more complete description of the gravimetric factor). This acceptor activity definition is quite useful when comparing various runs made with the same acceptor feed material, since by definition the full range of activities is from 0 to 1. However, when comparing runs where different acceptor materials were used, it is often more informative to eliminate the gravimetric factor, F_2, from Equation 5-54 and to redefine the activity as:

$$R = \frac{W}{C} \qquad (5-55)$$

where W and C are the same quantities described above. This value for the
acceptor activity readily permits intercomparisons of the reactivity (on a
weight basis) towards CO_2 of any acceptor material.

The standard method used for the determination of acceptor activity is de-
scribed in detail in Section 5.7 of this report, entitled Bench-Scale Support
Studies. In general, this measurement consisted of calcining a preweighed
acceptor sample at $1700°F$ ($927°C$) in a stream of prepurified nitrogen and re-
weighing the sample to determine the amount of CO_2 evolved. In addition to
this method, acceptor activities were often determined using the data ob-
tained from calcining the samples in a recording thermobalance (Stanton TR-1).
In this case, a sample (~ 1 g) was loaded into the thermobalance under 1 atm
of CO_2 gas and heated to $800°C$ ($1472°F$). Normally under these conditions a
recarbonated acceptor (gasifier boot sample) would maintain a constant weight.
After assurance that the sample had reached constant weight, the atmosphere
was changed to nitrogen and the sample was fully calcined. The sample weight
was constantly read out on a chart and the sample was calcined until constant
weight was achieved under 1 atm nitrogen at $800°C$. The activity was then
calculated by Equation 5-54 or 5-55. Normally the activities obtained by
both methods were in good agreement with each other; however, if discrepan-
cies were observed, the data gained by the first method was preferred due to
the approximate 20 fold larger sample size employed by that method.

The minimum acceptor activity required for the CO_2 Acceptor process gasifier
to be in heat balance is determined by two parameters. The first, acceptor
circulation rate, directly affects the sensible heat supplied by the acceptor
and indirectly influences the amount of chemical heat supplied by the accep-
tor. Since the acceptor activity declines in proportion to the number of
times it is cycled, increased circulation rate (at a constant rate of fresh
acceptor feed), while increasing the quantities of sensible heat from the cir-
culating acceptor, leads to decreased activity. The other factor which deter-
mines the minimum required activity is degree of CO_2 removal necessary for
achieving the desired ratio of H_2 to carbon oxides, for the final production
of methane. The minimum acceptable acceptor activity for the CO_2 acceptor
process is approximately R = 0.10, based on Equation 5-55. This is equiva-
lent to a dolomite-derived acceptor activity of about 0.26 and limestone ac-
ceptor activities of approximately 0.14, both based on Equation 5-54. Table
5-36 lists the equilibrium activity values obtained for the circulating ac-
ceptor during each of the pilot plant runs in which meaningful activity data
were obtained. This table gives the activity based on both Equations 5-54,
Column 17, and 5-53, Column 18 (see Table 5-36) where the Equation 5-54 grav-
imetric factors, F_2, used are : 0.390 for the early runs, and 0.365 for Run
45 with dolomite-derived acceptor, and 0.749 for all the runs employing lime-
stone acceptors. For the run with reconstituted acceptor (Run 47B), an F_2
value of 0.681 was used.

5.5.1   DOLOMITE-DERIVED ACCEPTORS

Rapid City pilot plant Runs 21, 26B, and 45 were successful runs, of suffici-
ent duration for complete change-out of the dead burned-dolomite start-up
material for fresh feed acceptor to be completed, in which dolomite-derived
acceptor material was used. A comparison of the data for these runs (Table
5-36) shows that the equilibrium acceptor activity maintained in Runs 21 and
26B were approximately the same. The equilibrium activity of the acceptor
from Run 45, however, was significantly lower than that of the two earlier
runs at ~ 0.15 vs. ~ 0.35. A great deal of this difference is undoubtedly
due to the significantly lower make-up rate employed in Run 45 (1.25% vs.
2.4-2.7%, Table 5-36, Column 5).

Table 5-36. RCPP BALANCE PERIOD RUN DATA

Run	Coal	Acceptor Circulation Rate lbs/hr	Acceptor Make-up Rate lbs/hr	Make-up Rate, % lbs Ca Fed/ lbs Ca Circulated x 100	Δt Gasifier min	Δt Boot min	Δt Regenerator min	Acceptor Activity $\bar{R}_{eq}$ CA Basis	Acceptor Activity $\bar{R}_{eq}$ Wt Basis
21-I	Velva Lignite	12150	560	2.40	13.5	3.7	52.9	0.320	0.122
21-II		11800	560	2.50	14.9	3.9	54.9	0.343	0.131
21-III		11130	560	2.61	18.0	4.0	60.2	0.300	0.115
26B-I		10980	560	2.70	29.8	4.1	56.2	0.364	0.142
26B-II		10980	560	2.70	29.0	4.1	53.8	0.392	0.153
28B		14570	560	2.03	11.9	2.7	38.8	0.132	0.099
33B		15040	560	1.98	11.7	2.5	35.5	0.142	0.106
38C	Wyodak Subbit.	12990	560	2.32	17.3	2.7	39.4	0.160	0.120
39	Glenharold Lignite	11750	700	3.29	19.4	3.1	46.2	0.220	0.165
40B	Texas Lignite	7664	840	6.02	27.7	4.6	64.7	0.218	0.163
45	Wyodak Subbit.	20700	560	1.25	12.0	2.0	16.4	0.150	0.055
46C	Velva Lignite	18300	270	0.76	6.6	2.3	21.8	0.105	0.078
47B		23420	268	1.03	8.4	1.8	14.3	0.091	0.062

Table 5-36. RCPP BALANCE PERIOD RUN DATA (continued)

Run	T Gasifier °F/°C	T Regenerator °F/°C	Ave P H_2O Atm Abs.	Ave CO_2 Driving Force Atm Abs.	Acceptor Material	Acceptor Activity R_{eq} CA Basis	Acceptor Activity R_{eq} Wt Basis	Particle Density $\bar{\rho}_{Acceptor}$ Recarbonated lbs/cu ft	Acceptor Feed Time (hr)
21-I	1480/804	1850/1010	3.66	.783	Tymochtee Dolomite	0.320	0.122	145	155
21-II	1480/804	1860/1016	3.69	.778		0.343	0.131	146	207
21-III	1480/804	1850/1010	3.28	.739		0.300	0.115	144	227
263-I	1495/813	1840/1004	3.35	.631		0.364	0.142	141	
26B-II	1495/813	1840/1004	3.35	.631		0.392	0.153	142	
28B	1490/810	1835/1002	3.56	.822	Rapid City Limestone	0.132	0.099	126	252
33B	1490/810	1845/1007	3.58	.821		0.142	0.106	122	133
38C	1515/824	1840/1004	3.44	.596		0.160	0.120	113	241
39	1490/810	1845/1007	3.30	.697		0.220	0.165	113	114
40B	1480/804	1835/1002	3.10	.774		0.218	0.163	111	139
45	1528/831	1843/1006	3.61	.619	Tymochtee Dolomite	0.150	0.055	143	200
46C	1490/810	1890/1032	4.55	1.126	Rapid City Limestone	0.105	0.078	142	178
47B	1510/821	1860/1016	3.17	.727	Reconstituted Acceptor	0.091	0.062	142	78

However, even after correction for the lower make-up rate* the equilibrium activity of the Run 45 acceptor is still well below that of the other dolomite-derived acceptor runs.

The make-up rate adjustment to the activity is based upon the data obtained from cycling samples of the acceptor in the automatic cycle test unit under various conditions, as described in Subsection 5.5.4 of this report. In essence, this method involves plotting the acceptor activity vs. number of cycles at each set of conditions and deriving equations which best fit the data. These equations are then used, via a computer program, to generate predicted equilibrium activity values for a given make-up rate of fresh acceptor. In general, the laboratory-generated activity data fit to the pilot plant data is excellent.

Table 5-37 shows a comparison between the calculated equilibrium activity, as described above, and the actual equilibrium activity measured during the pilot plant runs. The calculated activities in Table 5-37 are based on the following conditions:

$T_{Gasifier}$ = 1520°F (827°C); $T_{Regenerator}$ = 1840°F (1004°C); Gasifier Residence time = 30 min; Regenerator Residence time = 50 min; total pressure = 11.2 atm. absolute; steam pressure = 3.5 atm. absolute.

Examination of the data in Table 5-37 reveals that while the $\triangle R$ values for Run 21 and 26B all cluster around a $\triangle R$ of zero, the Run 45 values (-39.0) is well below the others. Since this observed activity difference must be due to some change in the operating conditions, a study of the process variables should be beneficial in explaining the lower than expected equilibrium activity of Run 45. The particular process variables which could possibly have an effect on the acceptor activity are: (1) bed temperature of the gasifier and regenerator, (2) bed residence times in both vessels, (3) steam partial pressure, and (4) total pressure. Early laboratory work has shown that the presence of other gaseous species such as CO, H_2O, and N_2 have no measureable effect on the acceptor activity pattern, hence these were not examined here.

Figure 5-20 is a plot of $\triangle R$ vs. each variable for the three Tymochtee dolomite-derived acceptor runs. The five scales at the bottom of the plot represent regenerator bed temperature, gasifier residence time, regenerator residence time, steam partial pressure, and gasifier bed temperature, respectively. It is apparent from this plot that the regenerator bed temperatures and the steam partial pressure are not correlated with $\triangle R$ in any recognizable manner. Alternatively, both bed residence times and the gasifier temperature seem to show a positive correlation with $\triangle R$.

The relationship between the gasifier residence time and $\triangle R$ is as expected from laboratory experiments on cycling dolomitic acceptors in the cycle test unit (see Subsection 5.5.4). The carbonation of these acceptors follows a pattern of rapid initial rate to about 90% of the saturation value, followed by a much slower rate which continues to completion. This trend is clearly borne out by the plant data in Figure 5-20. Apparently the gasifier residence time of 12 minutes in Run 45 was still

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* % make-up = $\dfrac{\text{lbs. fresh Ca fed}}{\text{lb. Ca circulated}}$ x 100

Run	Acceptor	$\overline{R}_{eq}$ Observed (Ca basis)	$\overline{R}_{eq}$ * Calculated (Ca basis)	ΔR^+
21-I	Tymochtee Dolomite	0.320	0.319	+.3
21-II		0.343	0.325	+5.4
21-III		0.300	0.331	-9.4
26B-I	$\longrightarrow$	0.364	0.336	+8.3
26B-II		0.392	0.336	+16.7
28B	Rapid City Limestone	0.132	0.144	-8.1
33B	$\longrightarrow$	0.142	0.144	+1.4
38C		0.160	0.145	+10.1
39		0.220	0.158	+39.4
40B	$\longrightarrow$	0.218	0.216	+9.0
45	Tymochtee Dolomite	0.150	0.246	-39.0
46C	Rapid City Limestone	0.105	0.107	-2.0

* Basis: $T_{Gasifier} = 827°C$

$T_{Regenerator} = 1004°C$

$\Delta t_{Gasifier} = 30$ min

$\Delta t_{Regenerator} = 50$ min

$P_{tot} = 11.2$ Atm

$P_{H_2O} = 3.5$ Atm

$$\Delta R^+ = \left[\frac{R_{Obs} - R_{Calc}}{R_{Calc}} \right] \times 100$$

Table 5-37.   CALCULATED VS OBSERVED ACTIVITY
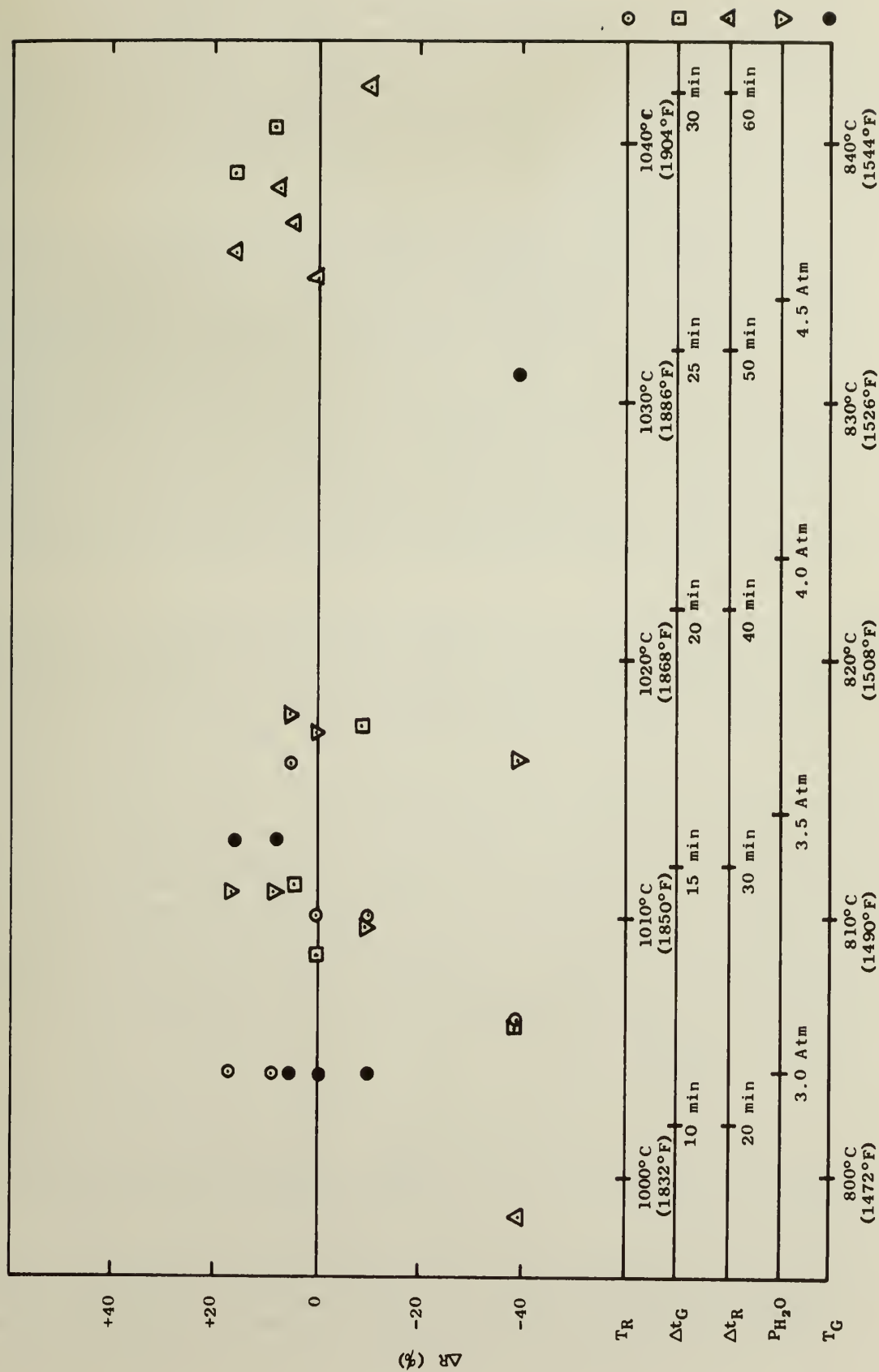
Figure 5-20. ΔR VS PROCESS VARIABLES (TYMOCHTEE DOLOMITE ACCEPTOR)

151

within the rapid initial phase of recarbonation, while the residence times in the other runs were sufficient to have passed this stage. The critical time for reaching this plateau region in actual plant operation can be estimated from Figure 5-20 to be about 13 minutes. Hence, for the use of dolomite-derived acceptor, gasifier bed residence times should be at least 13 minutes to ensure nearly complete recarbonation of the acceptor. Further increases above the critical 13 minutes would help to improve the activity, but to a much lesser extent. These conclusions are in total agrement with earlier predictions based on the laboratory cycle tester data.

The explanation for the apparent correlation of activity with gasifier bed temperature is more complicated than for that of the gasifier residence time. One possible reason, decreased CO_2 driving force (where the driving force is defined as the pressure of CO_2 over and above the equilibrium partial pressure), is virtually eliminated by the data on driving force in Table 5-36. Although the CO_2 pressure required for equilibrium was higher in Run 45, due to the higher gasifier temperature, the driving force is approximately the same as that in Run 26B. Hence, decreased driving force is probably not responsible for the observed trend. Perhaps the increased gasifier temperature enhanced the mobility of the calcium, as discussed in Subsection 5.5.4, resulting in a more rapid than normal rate of crystallite growth of CaO in the acceptor from Run 45, which would lead to the observed lower-than-anticipated activity for this run.

The data of Figure 5-20 also suggest a direct dependence of equilibrium activity on regenerator bed residence time. Such a phenomenon, if real, would be totally unexpected and could probably only be explained by a failure to fully calcine the circulating acceptor, which would allow a continued "soak" in CO_2 as calcium carbonate. This could allow for a more rapid buildup of large $CaCO_3$ crystals, which when finally calcined would yield large inert calcium oxide crystals. However, a careful examination of the regenerator samples from Run 45 revealed no significant signs of undercalcination of these samples. More likely, this apparent correlation is fortuitous. Probably a combination of the low gasifier residence time and high gasifier temperature is responsible for the large negative $\triangle R$. The laboratory experiments on the effect of regenerator residence time on activity suggest a small effect and in the opposite direction (i.e., a shorter residence time in the regenerator should improve the equilibrium activity of the acceptor). The laboratory data on the effect of variables on acceptor activity are discussed more fully in Subsection 5.5.4.

5.5.2   LIMESTONE ACCEPTORS

Runs 28B, 33B, 38C, 39, 40B, and 46C in the pilot plant employed Rapid City limestone as the acceptor material. The complete set of operating conditions and activity data for each of these runs is given in Table 5-36, and the comparison of calculated and observed activity is presented in Table 5-37.

The $\triangle R$ data in Table 5-37 clearly show that the activity of the acceptor in all the limestone acceptor runs except Run 39 are in good agreement with the predicted values. The activity of the Run 39 material, however, is quite a bit higher than anticipated from the laboratory correlation.

A plot of the ΔR values vs. the process variables, Figure 5-21, fails to show any real trends which are able to explain the increased acceptor activity in this run. All the variables shown in this figure seem to be randomly distributed and appear to have little influence on the activity. This is in agreement with the cycle tester data on Rapid City limestone acceptors, which also suggest that each of these variables has little or no effect on the acceptor activity pattern.

There were two features unique to Rapid City Pilot Plant Run 39 which may have had an influence on the acceptor activity. First is the fact that Glenharold lignite, a high-sodium content North Dakota lignite, was used as the feed coal for this run. Since this was the only pilot plant run using this coal in which heat and material balance data were obtained, it is conceivable that something inherent in this coal, or more likely the ash from it, was responsible for the increased activity.

The other difference between Run 39 and the other limestone acceptor runs was that the steam pressure in the gasifier boot was reduced from the normal value of $\sim$11.3 atm to $\sim$8.8 atm. This was done in order to prevent transient melt formation and agglomeration of the acceptor (see Subsection 5.5.4 for a more detailed discussion of this problem). Although the steam partial pressure was lowered (by dilution with gasifier recycle gas), the total system pressure and CO_2 partial pressure were virtually unchanged at 11.6 and 0.23 atm, respectively.

One plausible explanation for the higher than anticipated activity in Run 39 is that even with the reduced steam partial pressure some melting may have occurred which possibly could have enhanced the formation of $CaCO_3$. This may be an indication that low melting liquid systems, which are created when high-sodium lignites are gasified, might be useful in maintaining higher acceptor activity levels.

Finally, another possible reason for the relatively high acceptor activity of Run 39 is enhanced particle shell formation. If the use of the Glenharold high-sodium content lignite speeded up the process of shell formation, and if the shell material contained a fair amount of active calcium (calcium present as CaO and not calcium silicates), then it is conceivable that the finely divided inert material in the shell may act in a manner similar to that of the MgO in the dolomite-derived acceptor. This is to say that the activity decline in the shell material would be slower than that of the acceptor interior because of the effect of the inerts on Ca mobility, as discussed in Subsection 5.5.4. Since the effect of ash could not be tested in the cycle test unit, the effect of shell formation was not examined in the laboratory and hence was not taken into account in the correlations.

Run 46C was unique in its use of 12.6 atm total pressure versus the 11.6 atm employed in all other runs. While the acceptor activity from this run is consistent with that predicted from the cycle tester data, it is interesting to note that the particle density (142/lb cu ft) is considerably higher than that of the other runs in which Rapid City limestone was used as the acceptor (ave = 117 lb.cu ft). Since increased acceptor density aids showering through the gasifier char bed, a relatively high acceptor particle density
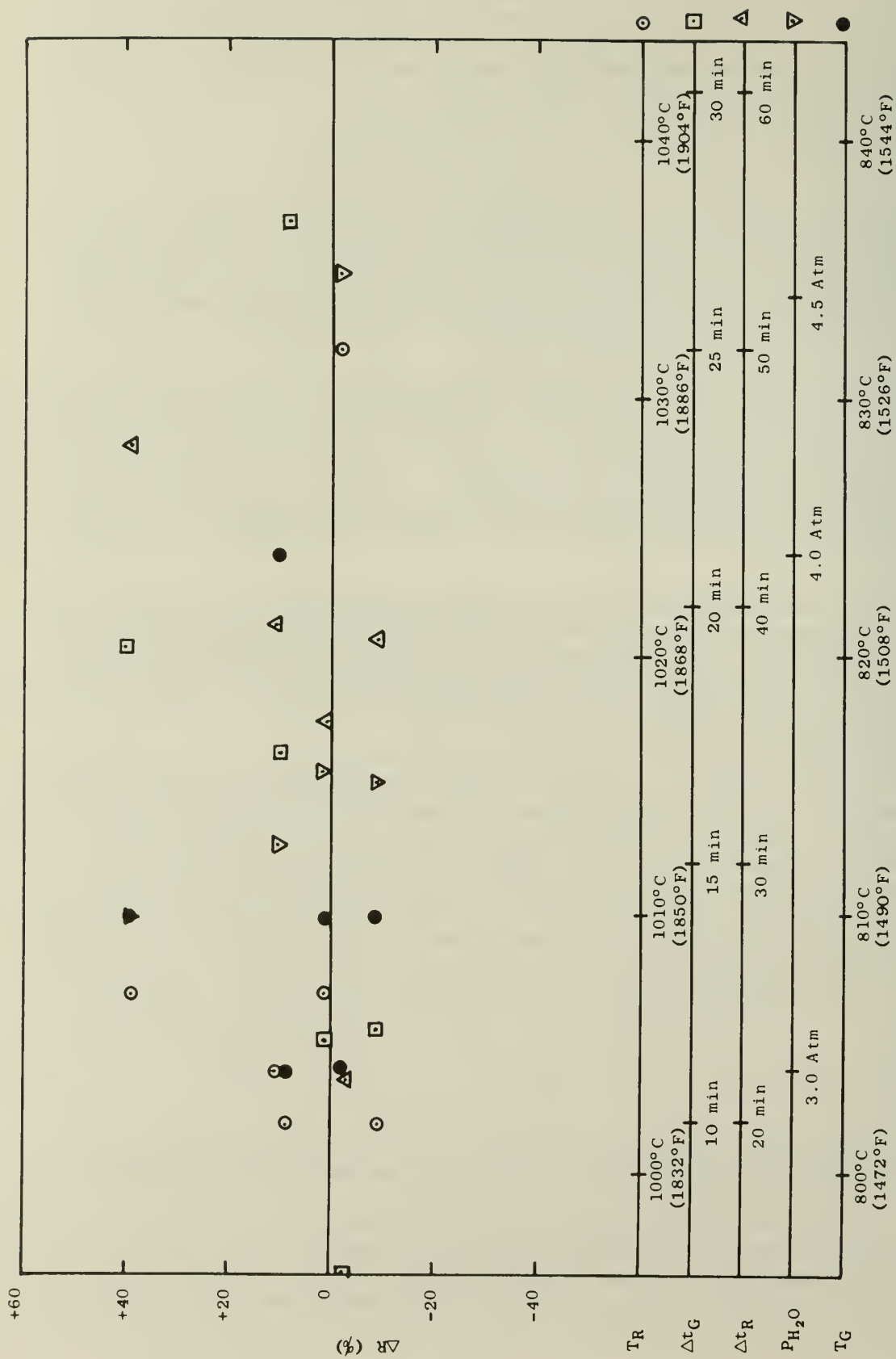
Figure 5-21. ΔR VS PROCESS VARIABLES (RAPID CITY LIMESTONE ACCEPTOR)

154

(such as that of the stone in Run 46C) is desirable. Hence, it could be beneficial to delineate the operating conditions in Run 46C which lead to the increased acceptor particle density.

Most likely, the increased total pressure and thus increased steam pressure in the gasifier (and particularly in the gasifier boot) led to a partial melting in the calcium oxide-calcium carbonate-calcium hydroxide ternary system, which resulted in the observed increased particle density. Microscopic examination of the acceptor from this run suggest that melting may have occurred in the shells of these particles. The outer layers of acceptor particles from Run 46C appear to be much more dense than those from any other run. Furthermore, there appears to be little or no microcrystallinity associated with the shells of these acceptor particles, in marked contrast to all other spent acceptors studied.

The particle interiors, on the other hand, appear little different than those of all other acceptors studied. This suggests that whatever melting which may have occurred probably only affected the outer layers of the particles. Perhaps the increased ash content in the shells is more conducive to melt formation than are the less contaminated particle interiors. Probably, as is suspected for Run 39 acceptor, the activity of the shell material in which melt formation has occurred is higher than that of the interior; however, for the Run 46C stones the shells are so dense that they may have acted as a physical barrier to recarbonation of the particle interiors. Hence, the shells may have been more active and the interiors less active than those of other acceptors, which may have led to an overall activity close to that predicted by the laboratory model data.

It is interesting to note that if partial melting of acceptor particles did occur during Run 46C, it did not lead to agglomeration of the particles in the gasifier boot. This is quite encouraging, as it suggests that the process may be operable under partial melt forming conditions even with natural limestone acceptors.

5.5.3   RECONSTITUTED ACCEPTORS

The final pilot plant run, Run 47B, was carried out using lime-rich material (reconstituted from spent limestone acceptor) as the acceptor feedstock. This reconstituted acceptor material was prepared by slaking spent limestone acceptor from Runs 39, 40B, 42, and 43 to effect a removal of the silica rich shell material, followed by pelletizing the recovered slaked lime via the Dorr-Oliver fluosolids lime recovery process. The actual preparation of the reconstituted acceptor is fully described in Section 6 of this report.

The process variable and acceptor activity data for Run 47B are also presented in Table 5-36. The activity of the reconstitued acceptor during this run (0.091 on a calcium basis) is quite low. This low activity is undoubtedly due, in part, to the very high circulation rate employed for this run, which in turn led to a relatively low fresh acceptor make-up rate. This, of course, increases the average age of the circulating stone and hence yields a lower equilibrium activity.

Due to the rather large variations in the composition of the reconstituted acceptor produced for this run, a direct comparison is unavailable with laboratory cycle tester data, as was done for the dolomite and limestone acceptors, above. However, the pilot plant activity
data for this run agree rather well with the laboratory data obtained
from cycling individual reconstituted acceptors from various periods
during the production run.

Aside from the rather low activity, the reconstituted acceptor seems
to be a very suitable feedstock to the CO_2 acceptor process. The almost
spherical particle shape is quite beneficial for maintaining high circulation
rates. The relatively high particle density (142 lbs/cubic ft) aids the
showering of acceptor through the char bed in the gasifier.

A possible drawback to the use of reconstituted acceptors commercially
is the extent of its reaction with ash; in other words, shell formation.
Shell formation was observed during Run 47B, but to a lesser extent than
when limestone acceptors were used with the same coal (Velva lignite).
Possibly the degree of shell formation will be low enough to permit the
expected reconstitution and use of acceptors; however, more data are needed
in this area.

5.5.4   FACTORS AFFECTING ACTIVITY

Several parameters which could have an influence on the performance of
the various materials used as CO_2 acceptors were examined. The variables
studied for their effect on acceptor activity were (1) the bed temperatures
of the gasifier and regenerator, (2) the total system pressure as well as
the partial pressures of the various gaseous components, and (3) the coal
used as feedstock in the process. These variables were studied by examination of the pilot plant run data and by various tests performed in the
laboratory.

A considerable amount of work was also carried out to explore ways in which
acceptor performance could be improved. This included such things as acceptor reconstitution, acceptor reactivation, and synthetic acceptor studies.

5.5.4.1   Laboratory Methods

5.5.4.1.1 Cycle Tester

The majority of the acceptor activity measurements and testing was carried
out in an automatic cycle test unit. This unit consisted of a vertically
suspended reactor 35 inches in length and 0.562 inch I.D. x 1.000 inch
O.D., Type 316 stainless steel, medium-pressure tubing enclosed in a
34 inch length of 1 inch, Schedule 40, Type 310 stainless steel pipe.
The reactor was closed at the top with a high-pressure tee and at the
bottom by a high-pressure elbow.

The two temperature zones (gasifier and regenerator), with centers located
12 inches apart, were heated via helically wound resistance heaters which
were independently controlled with temperature indicated controllers at

156

the desired temperature. The temperature along the length of the reactor was monitored via ten thermocouples attached to the outer walls. The temperature of each zone was normally controlled by the external thermocouple in the center of each 6-inch zone; however, when the sample was in either the high or low temperature zone, the temperature of that zone was controlled internally by the sample thermocouple.

The sample was raised and lowered between the two temperature zones by means of a pneumatically operated hydraulic piston with a 12-inch stroke. The operation of the piston as well as the gas flow and pneumatic valves was controlled by an automatic cycle timing clock.

The sample holder consisted of a Type 310 stainless steel frame and a 48 mesh stainless basket which held approximately 1 gm of acceptor sample. The holder unscrewed at the top to permit easy filling and replacement of the basket. The sample holder assembly was welded to a 1/4-inch Type 310 stainless steel tube which acted as a thermowell for the sample thermocouple, which was inserted into the sample through a hole in the top of the basket, as well as the pushrod for the hydraulic piston. The sample holder/thermowell/pushrod was sealed via a packing gland at the top of the reactor and a lava seal in the pushrod handle.

The assembly drawings for the reactor and sample holder are shown in Figures 5-22 and 5-23, while Figure 5-24 is a flow diagram for the operation of the entire cycle test unit.

A typical run in the cycle tester was carried out in the following manner: Approximately 1 gram of the material to be tested (normally sized 10 x 14 Tyler mesh) was weighed into the sample holder. The sample holder was then attached to the thermowell-pushrod and secured in the preheated reactor with the sample at the topmost (ie.e, coolest) position. The system was then pressurized in a carbon dioxide atmosphere. Finally, the run was begun by lowering the sample into the calcination (hot) zone and starting the timing sequence.

Upon initiation of a cycle the sample was held in the calcination zone of the reactor until the sample temperature had equilibrated at the desired calcination temperature, at which time the carbon dioxide flow was turned off and the calcination gas mixture was switched on. After a preprogrammed purge period, the calcination half-cycle timing was begun. The calcining conditions were maintained for the desired time interval, at the conclusion of which nitrogen gas was substituted for the calcination gas mixture.

The system was purged with nitrogen, then the sample was raised to the cooler recarbonation zone of the reactor. Upon equilibration of the sample at the desired recarbonation temperature, the nitrogen flow was stopped and the carbonation gas mixture (saturated with the desired steam content) was directed into the reactor. The sample was maintained at the desired recarbonation conditions for the desired time interval, after which a flow of CO_2 gas was substituted for the carbonation gas mixture flow. After a 1-minute purge, the recarbonated sample was again lowered into the calcination zone and the cycle was repeated.
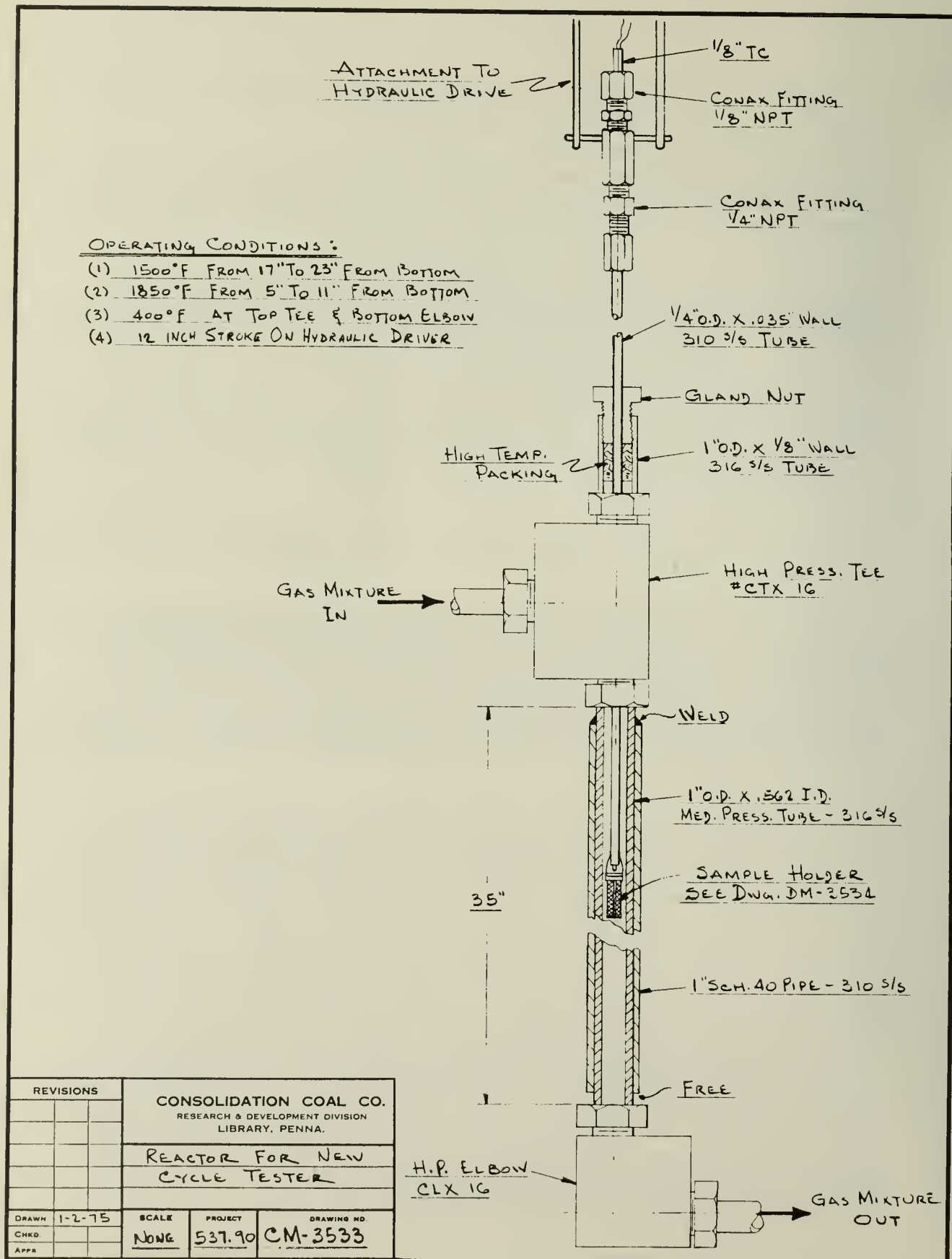
Figure 5-22. REACTOR FOR AUTOMATIC CYCLE TEST UNIT

CAP
310 S/S

28M. SCREEN - 316 S/S

1/2"φ

1/8"φ HOLE

COLLAR - 310 S/S

3/8"

28M SCREEN - 316 S/S

1"

1/16"φ RODS - 310 S/S
3 EQ. SPACED

1/8"

1/2"φ

BOTTOM RING - 310 S/S

28M SCREEN - 316 S/S
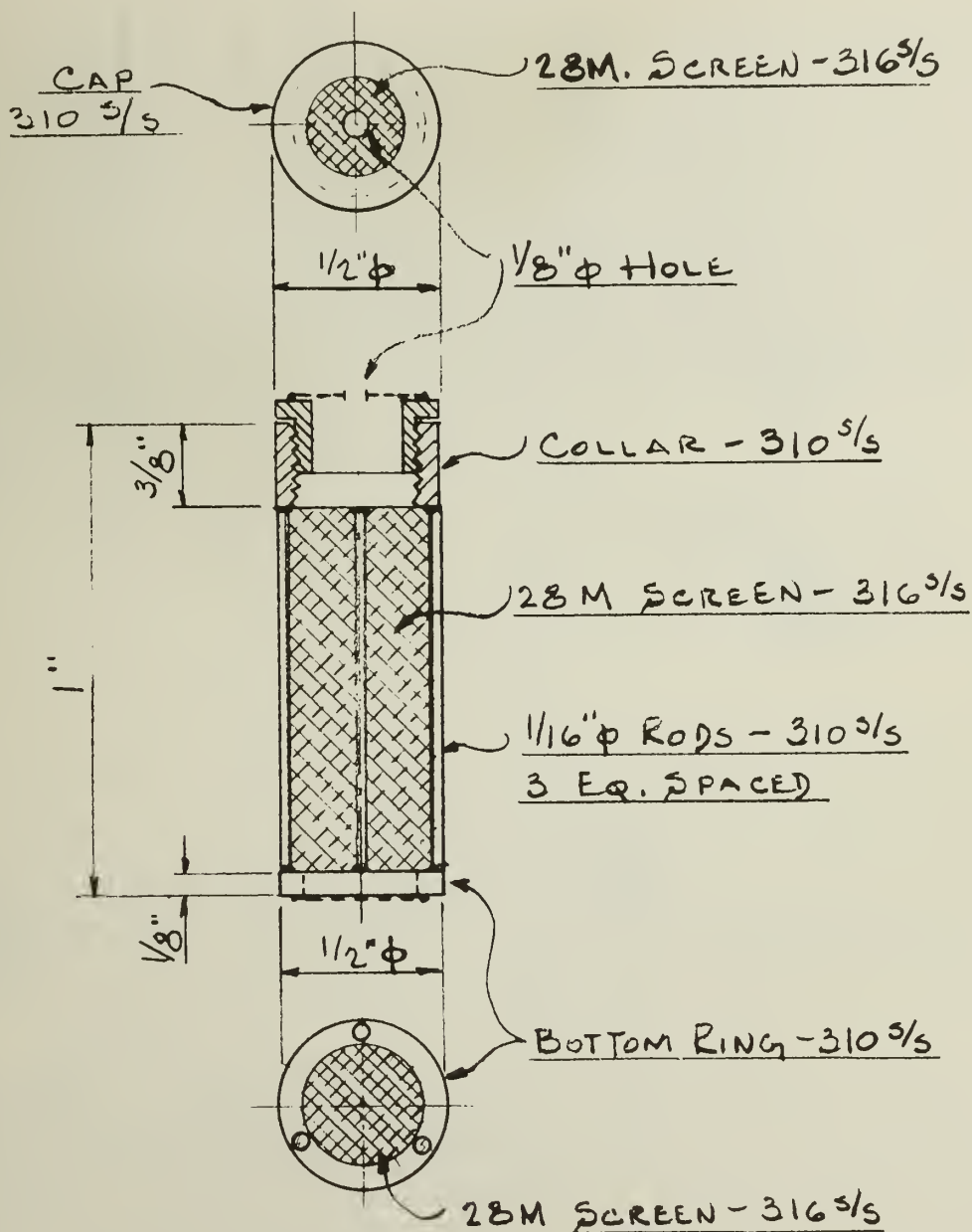
REV.	DATE			BY	APP.	CONSOLIDATION COAL COMPANY Research Division Library, Pa.

SAMPLE HOLDER FOR NEW CYCLE TEST REACTOR

BY	DATE 1-3-75	CHK.	APP.	PROJECT NO. 537.90	DWG. DM-3534

Figure 5-23. SAMPLE HOLDER FOR AUTOMATIC CYCLE TEST UNIT

159

Figure 5-24. FLOW DIAGRAM FOR AUTOMATIC CYCLE TEST UNIT

160

The sample activity could be measured at the conclusion of any cycle. The in-situ activity assay was accomplished in the following manner: When a cycle was completed, the sample was raised into the cool ($\sim 400^{\circ}$F) uppermost section of the reactor where it was allowed to cool in an atmosphere of CO_2 gas. After the sample had cooled, the whole system (exclusive of the saturator, which was isolated by a double valve) was evacuated and purged with nitrogen gas. This procedure was repeated three times to ensure that all traces of CO_2 had been removed. A preweighed bulb filled with ascarite, in series with a bulb of magnesium perchlorate, was connected to the system downstream of the reactor. After 15 minutes of nitrogen purge, the ascarite bulb was weighed to be sure no trace of CO_2 remained in the system. The assay was completed by lowering the sample into the calcination zone and collecting quantitatively in the ascarite bulb the CO_2 evolved. This method permitted continuous monitoring of the sample activity and avoided the possible effects of air-slaking during the sample handling, which otherwise would have been required.

5.5.4.1.2 Calculation of Equilibrium Acceptor Activity

The activity data obtained from runs in the automatic cycle tester were used to generate plots of activity vs. number of cycles, which in turn demonstrated the activity pattern for a given acceptor under a specified set of conditions. In general, log-log plots of this data yielded one or two straight lines, the equations for which could be used to describe the acceptor activity under the prescribed conditions.

With equations for activity and hence a knowledge of the cycle-by-cycle activity pattern for a given acceptor under a specified set of conditions, it is possible to calculate the equilibrium activity of an acceptor in a system where fresh make-up acceptor is added to and circulated acceptor removed from the system at a known rate. A computer program was written which calculated the fraction of the circulating acceptor which had been exposed to N cycles (N-1, N-2 etc.) down to the fraction that had just been added (i.e., the make-up fraction), where N was chosen large enough that the activity (when calculated to five decimal places) did not change between the N-10 and N+10 cycles.

After calculating these fractions, the program then summed the products of each fraction times the calculated activity for the number of cycles of that fraction. This sum is the mean activity of the circulated acceptor and, at a sufficiently large number of cycles, represents the equilibrium activity (i.e., the point where the removal of a portion of the circulating acceptor and addition of an equal quantity of fresh acceptor does not change the measured activity of the circulating inventory). In general, as was discussed in Subsections 5.5.1 through 5.5.3, the predicted equilibrium activities match the pilot plant data fairly accurately.

5.5.4.1.3 SEM-X-Ray Studies

A great deal of information on acceptor activity was obtained through the use of various microscopic and x-ray techniques. The physical and chemical examination of spent acceptors from the pilot plant gave a valuable insight into such things as the mechanism of deactivation and the properties of shell formation.

161

The most valuable techniques employed were the combination of scanning electron microscope (SEM) coupled with an energy dispersive x-ray analysis system and the Electron Microprobe-wave length dispersive x-ray system. These both provided much information on acceptor microstructure, crystallite size, and chemical makeup. X-ray diffraction studies were quite useful for the determination of the mineralogic species present in the various materials studied. This technique was especially valuable for determining the makeup of shells which formed on the acceptor particles during their circulation in the pilot plant.

Acceptor samples were prepared for SEM and microprobe examination by mounting a freshly broken particle on an aluminum sample holder with a conducting cement. The mounted particles were then either loaded directly into the vacuum chamber of the instrument or coated with a conducting layer (usually sputtered gold) and then loaded into the microscope. The individual particles were scanned until the desired features and details were seen; then, photomicrographs were taken of the area being examined. Finally, if desired, x-ray images of the area were photographed.

5.5.4.2   Crystallite Size vs. Acceptor Activity

The single most important reason for the decline in acceptor activity upon cycling in the pilot plant is the growth of large, relatively inert CaO crystals. The tremendous growth of CaO crystallites is clearly shown in the photomicrographs of Figures 5-25 and 5-26. These are comparisons between freshly calcined dolomite (Figure 5-25A) and spent dolomite-derived (Figure 5-25B) acceptor and a similar comparison for limestone acceptors (Figures 5-26A and 5-26B). The "before-and-after" nature of these pictures is quite revealing of the extent of crystallite growth which occurs during acceptor cycling in the pilot plant. It also should be noted that approximately the same degree of crystallite growth was observed in acceptors which were cycled in the automatic cycle test unit under simulated pilot plant conditions.

It should be pointed out that the rate of CaO crystallite growth is much more rapid in the limestone acceptors than in those derived from dolomite. This fact undoubtedly explains the slower rate of activity decline which is observed for dolomite-derived acceptor as compared to the limestone acceptors. Also of interest is the fact that while such spectacular growth of the CaO occurs in the dolomite-derived acceptors, the crystal size of the magnesium oxide is almost unchanged (Figure 5-25).

The fact that the calcium crystals grow to much larger sizes than the magnesium is somewhat surprising and indicates that the calcium ions in the dolomite-derived acceptor are considerably more mobile than the magnesium ions. A possible reason for increased calcium mobility may be the cyclical change of its chemical state during use in the CO_2 acceptor process. The result of periodic calcination-recarbonation may be the enhanced clumping together of the calcium while the relatively inert MgO remains essentially fixed in its original position.
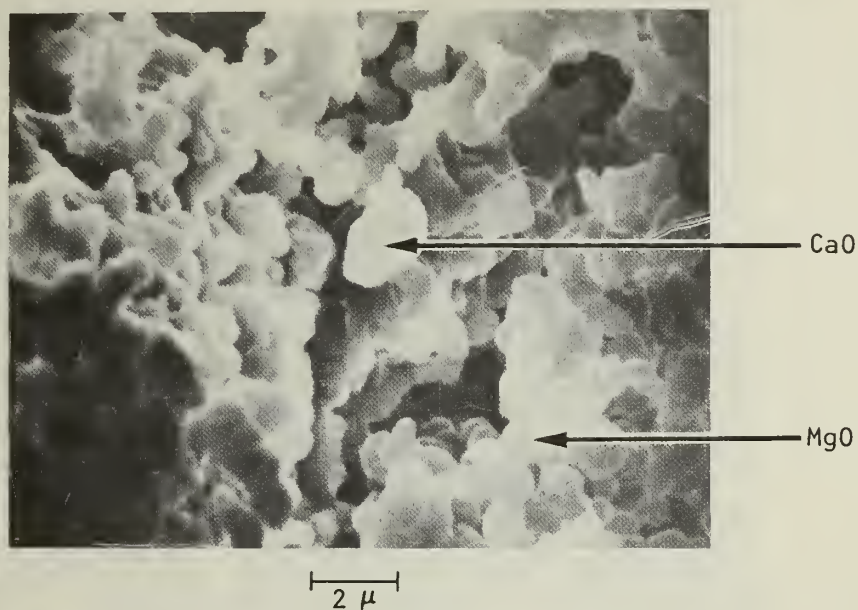
5-25A. FRESH ACCEPTOR
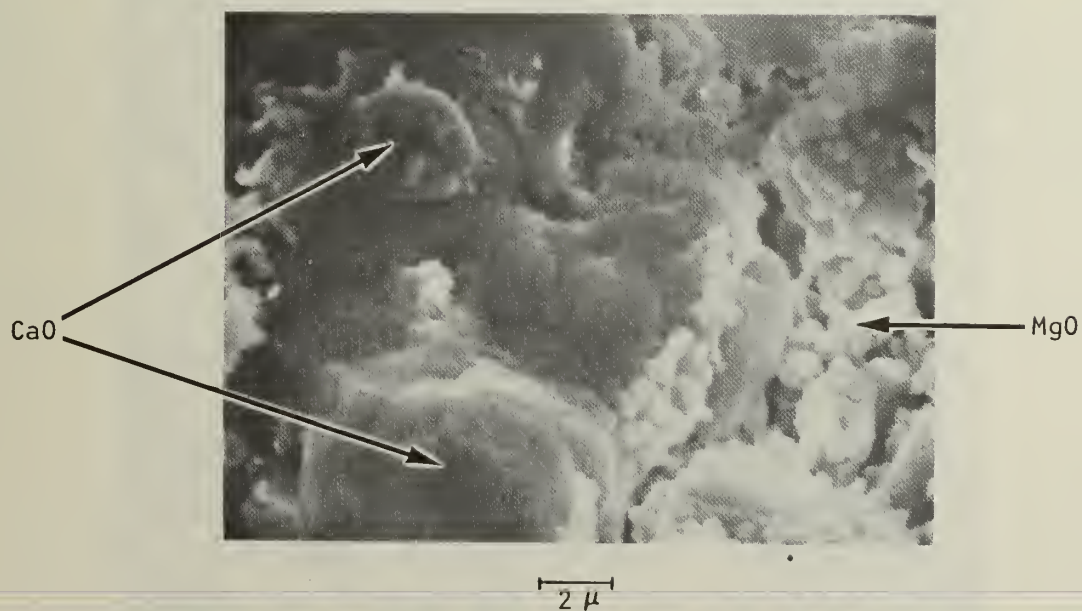
5-25B. SPENT ACCEPTOR

Figure 5-25. FRESH AND SPENT DOLOMITE - DERIVED ACCEPTOR (5000X)

163

5-26A. FRESH ACCEPTOR $\overline{10\,\mu}$
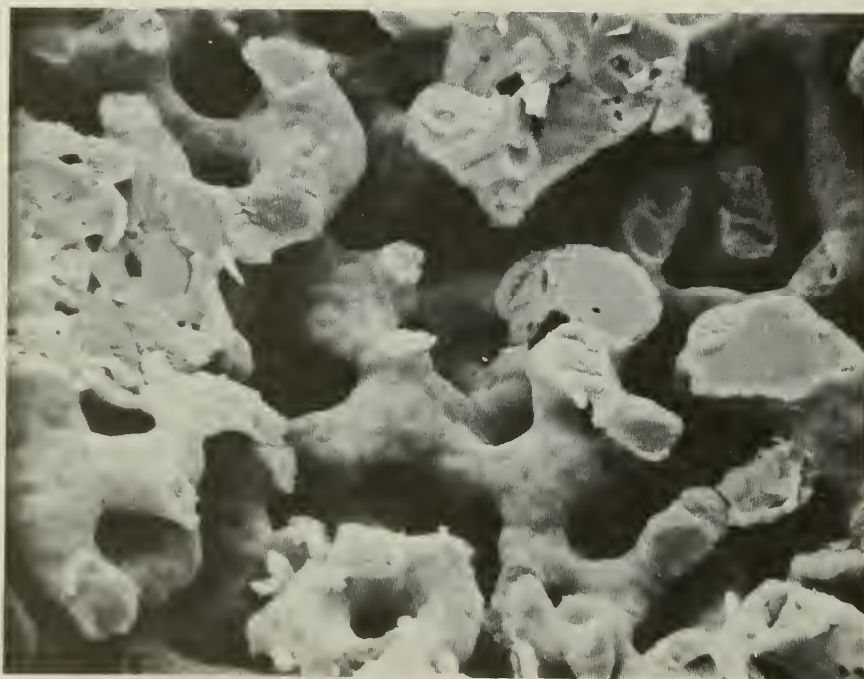
5-26B. SPENT ACCEPTOR $\overline{10\,\mu}$

Figure 5-26. FRESH AND SPENT LIMESTONE ACCEPTOR (1000X)

164

Microscopic examination of the calcium-bearing phases in the interior of these acceptor particles has revealed a possible mechanism for the growth of the CaO crystallites. Apparently if calcium oxide crystals are located within a certain minimum distance from each other, they are able to form a single calcium carbonate crystal upon exposure to carbonate forming conditions. The interparticle bridge or "necks" formed via this recarbonation mechanism remain fixed upon calcination and continue to grow in size with each recarbonation-calcination cycle, finally resulting in the massive crystals observed in interiors of the spent acceptor particles.

The effect of this crystallite size growth on acceptor activity is, of course, very adverse. As the particle dimensions increase, the kinetics of carbonation become increasingly slower. This is due mainly to poor diffusion of CO_2 through the surface layer of $CaCO_3$ which builds up initially on the CaO crystal surface. Due to the larger molecular volume of the $CaCO_3$ as compared to that of CaO, a higher density outer shell of $CaCO_3$ forms on the large CaO crystals, which inhibits further CO_2 diffusion and $CaCO_3$ formation; hence, the acceptor activity declines.

Figure 5-27A shows a broken surface of a spent limestone acceptor particle taken from the gasifier boot of the Rapid City pilot plant. The accompanying x-ray image (Figure 5-27B) shows the distribution of carbon in this "recarbonated" acceptor. The carbon (and hence, implied carbonate) buildup on the crystal surfaces is quite evident, as is the lack of significant carbonate in the crystallite interior. The size of the $CaCO_3$ layer on the CaO crystals of this micrograph suggest that when the calcium oxide crystals reach a size of $\sim 5\mu$ ($\sim$ twice the $CaCO_3$ layer thickness observed) or larger, significant inhibition of recarbonation (hence, loss of activity) will occur.

This crystal growth via carbonate linkage formation may also help explain the slower decay in activity which was observed for dolomite-derived acceptors in the pilot plant. In dolomite-derived acceptors the MgO acts as a diluent for the CaO + $CaCO_3$ and must, at least to some extent, inhibit the mobility of the calcium crystallites. Hence, in dolomite-derived material the MgO inhibits the clumping together of the calcium during re-carbonation and therefore retards the decay of acceptor activity.

The main conclusion of this work is that the observed activity loss for all acceptors in the CO_2 acceptor process is, for the most part, due to the crystallite size growth phenomenon.

5.5.4.3 Acceptor-Shell Formation

Early in the pilot plant program, it became apparent that "shells" of varying thickness were forming on the circulated acceptor particles. These shells were formed on both limestone and dolomite-derived acceptor and were present, to some degree, in every pilot plant run. The formation of the shells was definitely correlated with acceptor age, with the buildup apparently continuing throughout the life of the acceptor particles. The shell buildup was certainly dependent upon the particular carbon source (i.e., coal) employed and was almost nonexistent when subbituminous coal or Texas lignite was the feed material to the gasifier.
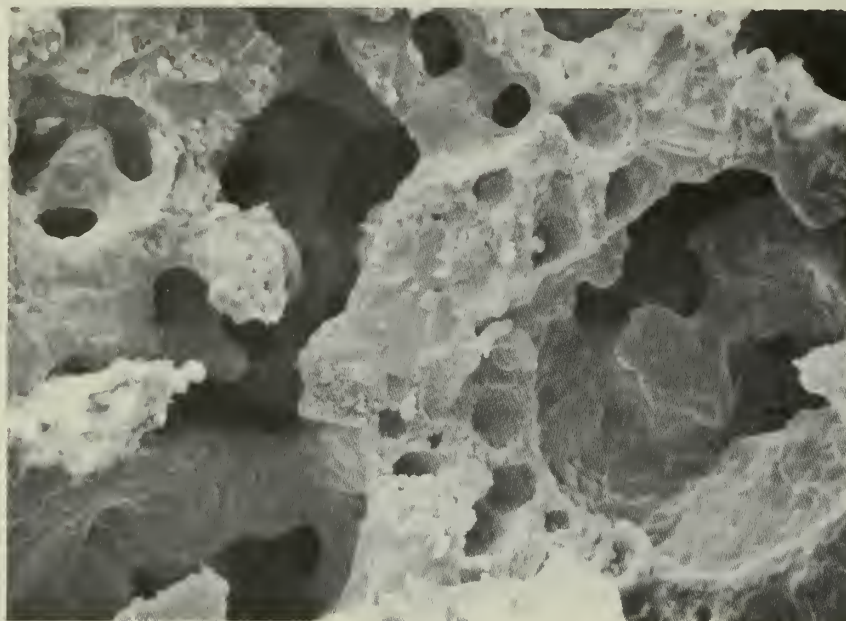
5-27A. BSE IMAGE   10 μ
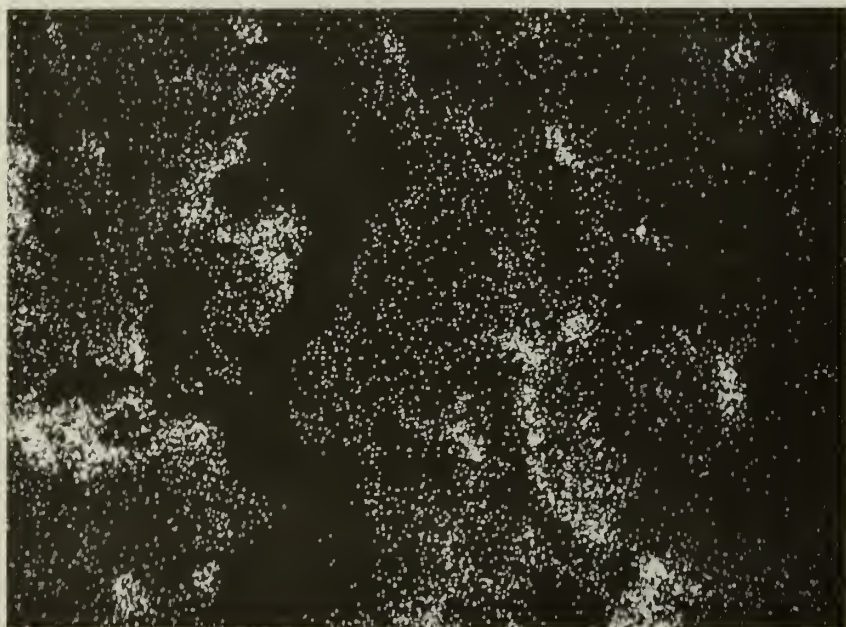
5-27B. CARBON X-RAY   10 μ

Figure 5-27.   INTERIOR OF RECARBONATED LIMESTONE ACCEPTOR (1000X)

166

The micrographs in Figure 5-28 are representative of "old" acceptor particles from RCPP runs where Velva lignite was used as the feedstock. Figure 5-28A, with a magnification of 100X, shows three important features of these acceptors: First is the smooth particle surface, which is quite thin (1 micron thickness) and appears to have been at least partially annealed. This type of smooth exterior is typical of all limestone acceptors used in runs with Velva lignite. The next feature, as one looks inward from the surface, is the particle shell. The shells of these acceptors are relatively fine grained and composed mainly of lime (CaO), with measurable amount of periclase (MgO), mayenite 12 CaO·7 Al$_2$O$_3$), and spurrite (Ca$_5$Si$_2$O$_8$CO$_3$). Figure 5-28B, at 200X magnification, also shows the relatively fine grained shell structure. The final gross textural feature of these acceptor particles is the interior. Seen in all three of the Figure 5-28 views, it is apparent that the particle interior is much coarser grained than the shell material. The large dimensions of the crystallites, almost entirely CaO, in the particle interior is probably responsible for the low activity of cycled limestone acceptors. It is interesting to note that although the shell material contains a lower percentage of calcium than the particle interior, the activity of the two materials are about equal. This is probably due to the finer grain size of the shell material, which would allow for better carbonation kinetics than the coarse grained interior.

The three micrographs in Figure 5-29 are of acceptor from RCPP Run 36, in which the high-sodium, Glenharold lignite was the carbon source. In Run 36, as in all the Glenharold lignite test runs prior to Run 39, the acceptor showed a strong tendency to agglomerate in the gasifier boot. Superficial examination of these agglomerates suggested that a partial melting of the shells had occurred, which led to particle agglomeration in the boot. Figure 5-29B, which shows the surface of a Run 36 acceptor particle, confirms this melting hypothesis. The surfaces of all the Run 36 acceptor particles examined on the SEM appear to have been at least partially molten at some time in their history.

The most likely reason for melting of the acceptor shells when high-sodium content lignite was used is a slightly different shell composition, caused by differences in the composition of the Velva and Glenharold lignite ash from which the shells presumably derive. A series of experiments were carried out to determine what combinations of boot temperature and gas composition (if any) would permit circulation of this acceptor without agglomeration. Table 5-38 presents a summary of the data obtained in these experiments for temperatures of 1400°F, 1450°F, and 1500°F and steam partial pressures of 9, 10, and 11 atm. For comparison, samples of RCPP Run 33B (Velva lignite feed) acceptor were also tested and the results of this work are presented in Table 5-39.

The data obtained in the above experiments suggest that lowering the partial pressure of steam to at most 10 atm or raising the temperature over 1500°F would probably eliminate the acceptor agglomeration problem when high-sodium lignite is used as the feedstock. This hypothesis was tested and confirmed by RCPP Run 39 in which Glenharold lignite was gasified with a reduced steam partial pressure in the boot. No acceptor agglomeration was observed in about seven days of operation of this run.
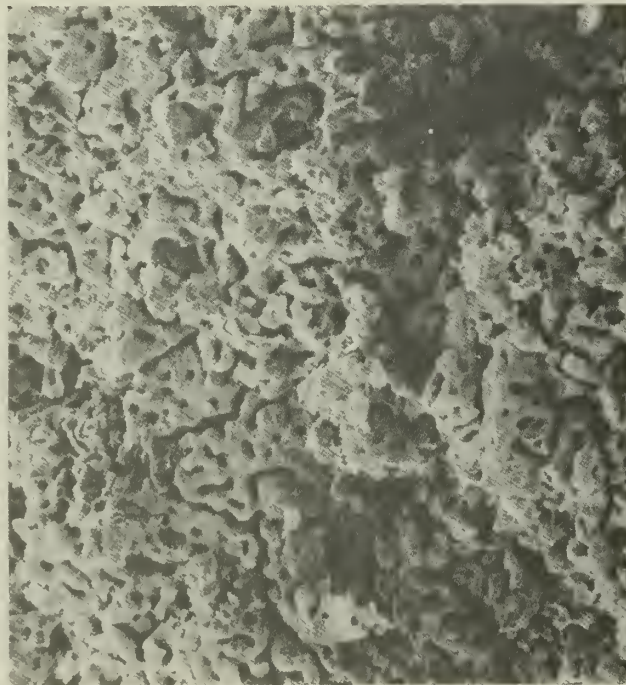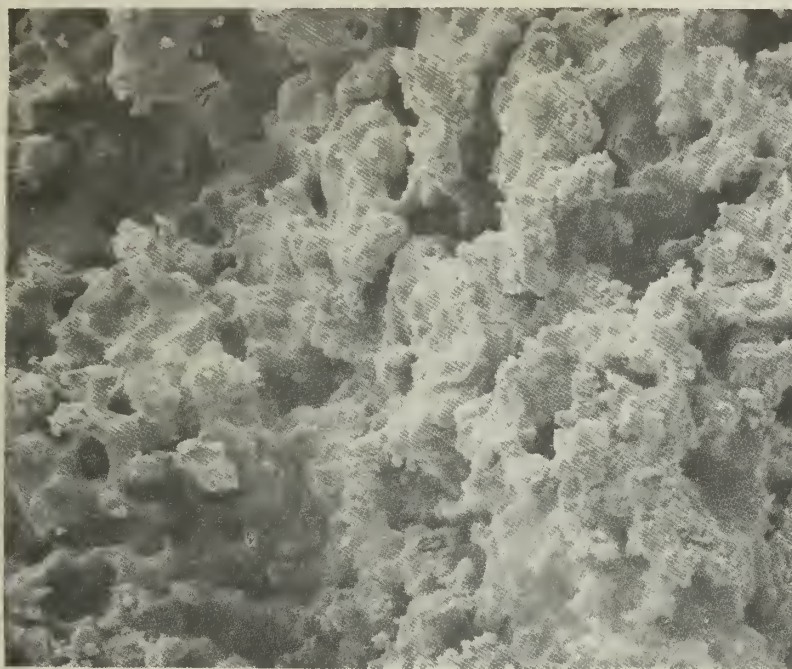
PARTICLE EXTERIOR

5-28A. SHELL |‾‾‾‾| 100 μ INTERIOR   5-28B. SHELL |‾‾| 50 μ INTERIOR
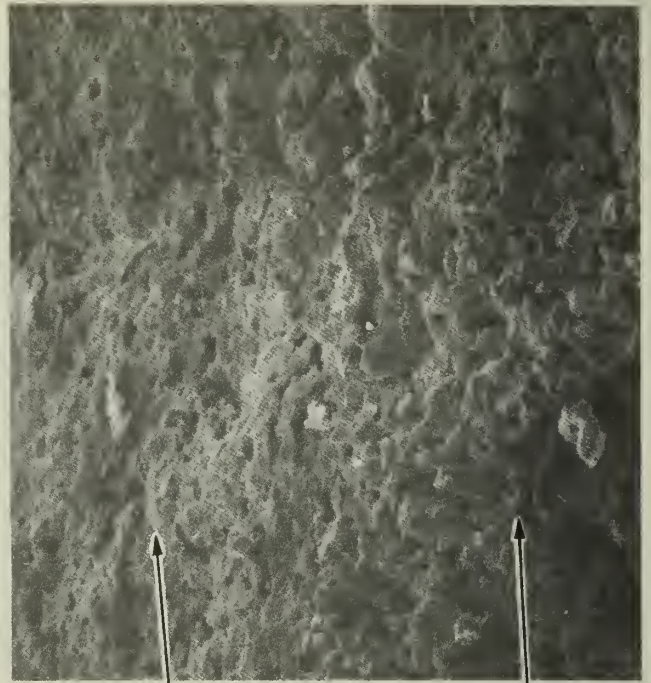
5-28C. INTERIOR

Figure 5-28.   RCPP RUN 33B CYCLED LIMESTONE⁻ACCEPTOR

168
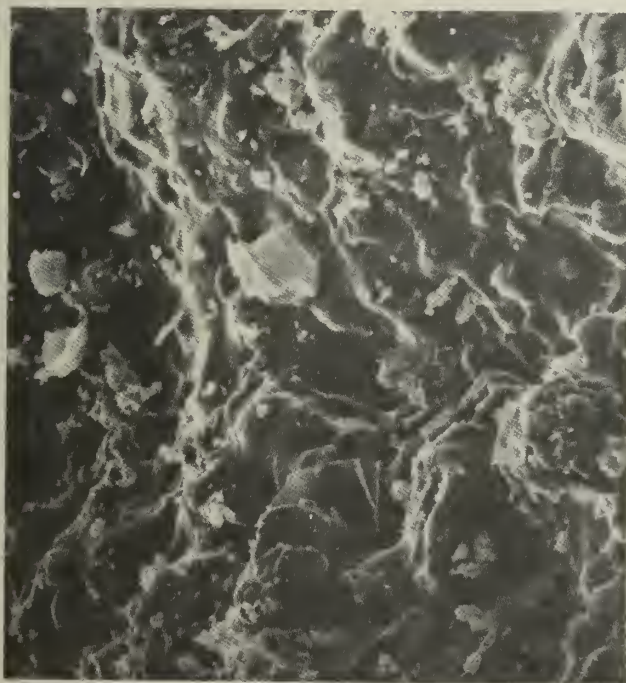
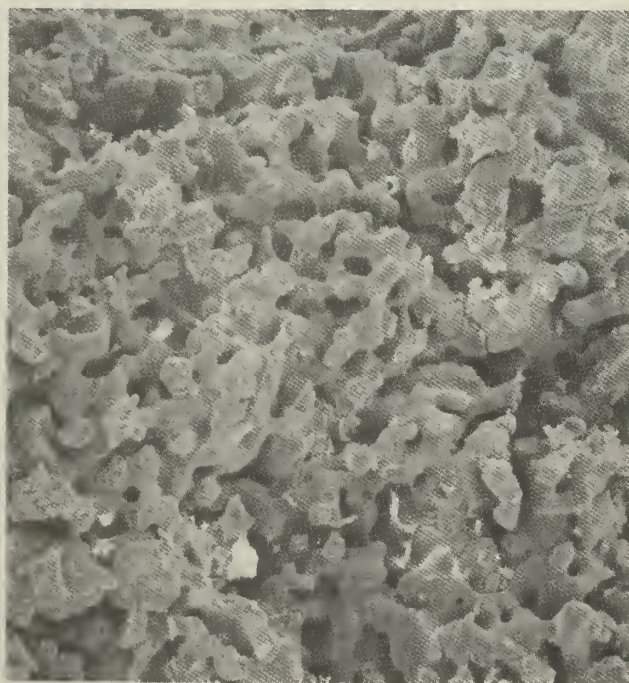5-29A.   INTERIOR |‾40 µ‾| SHELL

|‾40 µ‾|
5-29B.   PARTICLE SURFACE   5-29C.   PARTICLE INTERIOR

Figure 5-29.   RCPP RUN 36 CYCLED LIMESTONE ACCEPTOR - 250X

169

Temperature, °F	P_{H_2O} (Atm)		
	9	10	11
1400	O	-	-
1450	+	O	-
1500	+	+	Nominal RCPP Boot Conditions O

Table 5-38.   EFFECT OF STEAM PARTIAL PRESSURE AND TEMPERATURE
ON AGGLOMERATION OF RCPP - RUN 36 ACCEPTOR*

Temperature, °F	P_{H_2O} (Atm)		
	9	10	11
1400	+	+	-
1450	+	+	O
1500	+	+	+

*   + = Little or no agglomeration.
   O = Some tenuous agglomerates formed.
   - = Sample mostly glued up - almost totally agglomerated.

Table 5-39.   EFFECT OF STEAM PARTIAL PRESSURE AND TEMPERATURE
ON AGGLOMERATION OF RCPP - RUN 33B ACCEPTOR*

The two remaining pictures in Figure 5-29 show the similarities between the Run 36 and 33B acceptors. Figure 5-29A shows the more dense, finer grained shell structure which was also seen in Figure 5-28B for the Run 33B sample, while Figure 5-29C shows the coarse grained-large pore size interior which is quite similar to the particle interiors observed for Run 33B acceptor in Figures 5-28B and 5-28C. Hence, the only structural difference seen in the two acceptors is the outermost layer of shell which appears to have been melted in the Run 36 acceptor.

X-ray diffraction studies of the Run 36 acceptor shells revealed the presence of the same minerals that were found in the Run 33B material, in about the same proportion. Further, no sodium bearing minerals were detected in either the x-ray diffraction study or in the microprobe work, although a rather thorough search for sodium was conducted. This result was somewhat surprising and implied that some property of the Glenharold lignite ash, other than its high-sodium content, may have been responsible for the observed acceptor agglomeration differences between the Run 33B and Run 36 acceptors. However, chemical analyses of the acceptor from Runs 33B and 36 showed that the latter consistently contained more sodium than the former. Probably, use of the higher-resolution electron microprobe instead of the SEM for the study of the Run 36 acceptor material also would have shown the presence of sodium in the particle shells.

Additionally, more low melting point, sodium-bearing compounds may have been present on the particle surfaces. These compounds may have melted under the high steam pressures in the gasifier boot and then been volatilized in the regenerator on each successive cycle. This could explain both the melted appearance of the surface and relatively low sodium content of the shell material.

The three photo micrographs in Figure 5-30 are of cycled acceptor from RCPP Run 38A. Wyodak subbituminous coal was used as the carbon source in this run, and the acceptor particle density remained quite low throughout the run (and in subsequent runs with this feed coal).

Under microscopic examination the reason for the low density became apparent; however, the cause is still uncertain. The outstanding microscopic difference between acceptor from Run 38A and Run 33B is the almost complete lack of shell in the Run 38A material. It is known from all the microscopic studies made on RCPP cycled limestone acceptors that the shell material is finer grained and less macroporous than the particle interiors (see Figures 5-28 and 5-29); hence, the density of this material is probably higher than that of the interior. It is concluded, therefore, that the low particle density of the Run 38A acceptor is directly attributable to the lack of shells in these particles.

The reason for the observed lack of shells on the Run 38A acceptor is unknown. Acceptor shells are believed to be a reaction product of the calcium in the acceptor and the coal ash; hence, since the limestone used as acceptor was the same for all runs, the failure to form shells on Run 38A acceptor is probably due to some difference between lignite and subbituminous coal ash.
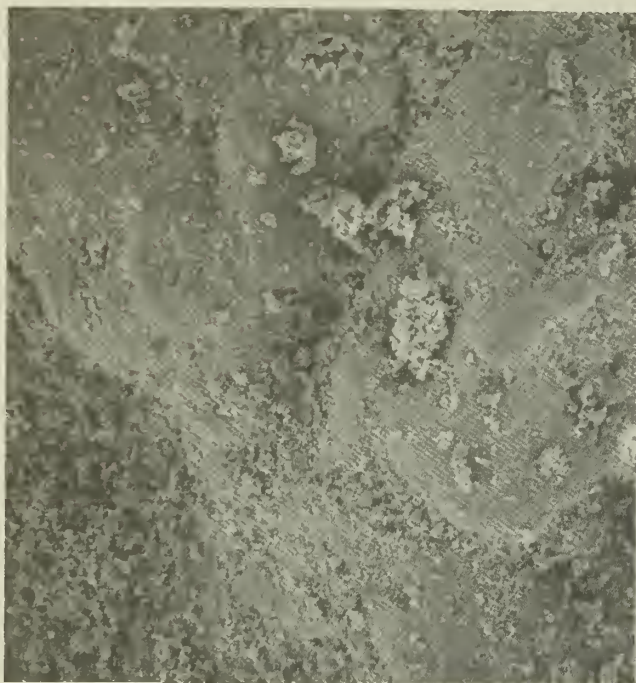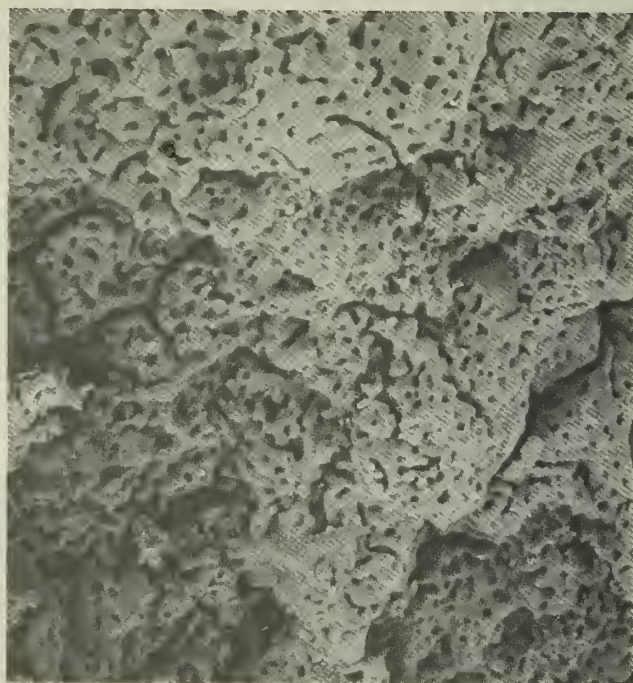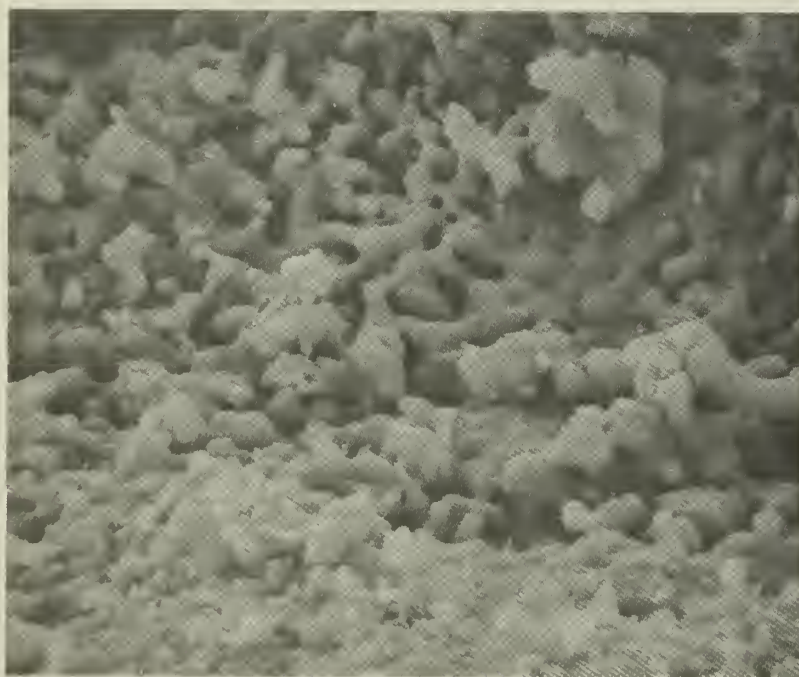
5-30A. SURFACE - 250X

5-30B. INTERIOR - 250X

5-30C. SURFACE - 2500X

Figure 5-30. RCPP RUN 38A CYCLED LIMESTONE ACCEPTOR

172

The lack of shell seems to be the only structural difference between the Run 38A and Run 33B acceptor. Figures 5-30A and 5-30C show the outer surface of the Run 38A material to be quite similar to the surfaces of the Run 33B acceptor (Figure 9A), as are the particle interiors (Figure 5-30B vs. Figures 5-28B and 5-28C.

The microstructure of spent dolomite-derived acceptor is quite similar to that of the limestone acceptors. The shells of the two are visually very hard to distinguish from each other, as are the particle surfaces. The x-ray microprobe reveals the fact that the magnesium content of the shells of dolomite-derived acceptor contain more magnesium than the limestone acceptor shell. However, the calcium-to-magnesium ratio in the shells of dolomite-derived acceptor is higher than that of the interior. This may be due to either of two reasons and more likely to a combination of both. The ash, which presumably reacts with the lime in the acceptor to form the shell, has a greater Ca/Mg ratio than dolomite; hence, the Ca/Mg ratio in shell is higher than in the particle interior. Secondly, the greater mobility of the calcium, as discussed earlier, may permit a gradual diffusion of Ca from the particle interior to the surface where it reacts with the ash to form the shells.

5.5.4.4   Effect of Process Variables on Acceptor Activity

A study of the effect of process variables on the acceptor activity was initially undertaken in order to see what changes could be made (if any) in the pilot plant operation to increase the acceptor equilibrium activity. Any modification of the process operation which could yield increased acceptor activity would be economically desirable, due to the reduction in fresh acceptor makeup which would be possible under those circumstances.

The effect of the partial pressure of steam, CO_2, N_2, CO, and H_2 on activity as well as that of particle size were determined in the following manner: Approximately 0.5 gm of acceptor was assayed for activity in the thermobalance, then loaded into the sample holder and placed into the "cool" ($<1000°F$) top zone of the continuous cycle tester. The cycle tester was then brough up to the desired operating pressure and the cycle was begun. In all the experiments described here, the initial part of the cycle consisted of a calcining step at $1840°F$ ($1004°C$) in a mixture of 19.3% CO_2 and 80.7% N_2.

Upon completion of the calcination step, the sample was raised into the "gasifier" zone of the cycle tester and held there at $1520°F$ ($827°C$) in the presence of the preselected gas mixture for the desired length of time.

Most samples were run for only one cycle, however, when more than one cycle was desired the sample was simply raised and lowered between the regenerator and gasifier zones.

As soon as possible after each run the sample was assayed for activity by calcination in the thermobalance.

5.5.4.4.1 Effect of Steam Partial Pressure on Activity

Five runs (1-5, Table 5-40) were made to determine the effect of P_{H_2O} on the acceptor activity. The acceptor used in these runs was the 8 x 10 mesh fraction of a sample taken from the gasifier boot at Rapid City during Run 19 in July, 1974. All five units were made at nominally the same conditions, with the exception of the partial pressure of steam (from 1 to 10 atm) and the total pressure (2 to 11 atm).

A plot (Figure 5-31) of P_{H_2O} vs. increase in activity, ΔR, shows that up to about 5 atm of H_2O the degree of reactivation strongly depends on the steam pressure. However, above this pressure little or no increase in ΔR is observed with increasing P_{H_2O}.

5.5.4.4.2 Effect of Partial Pressures of CO_2 and Other Gases on Activity

A comparison of the activities of samples run at 0.43 and 1.12 atm of CO_2 (Runs 6 and 7, Table 5-40) indicate that the partial pressure of CO_2 has little or no effect on the activity as long as the P_{CO_2} is significantly higher than the required driving force (~ 0.35 atm at 1520°F). The larger ΔR in Run 7 is probably due to the higher P_{H_2O} (3.6 atm vs. 2.9 atm).

Runs 1 and 8-10 (Table 5-40) were conducted to check what effect, if any, the presence of the gases other than H_2O and CO_2, which are present in the gasifier at Rapid City, would have on the degree of reactiviation. These data show that N_2 alone has no effect on reactivation, while the presence of CO and H_2 may slightly enhance the acceptor activity. These data also are plotted on Figure 5-31.

5.5.4.4.3 Effect of Particle Size on Activity

Runs 11-16 of Table 5-40 were made specifially to determine the effect of particle size on the degree of reactivation. An aliquot of hand-picked "old" stones from the gasifier boot in RCPP Run 19 was crushed in a mortar and pestle and separated into the size fractions indicated. Each size fraction, together with the original 8 x 10 starting material, was treated in the cycle tester under nominally the same conditions of temperature, pressure, and gas composition.

From a plot of ΔR vs. size (Figure 5-32) of these data, one finds that the smaller size fractions are more fully reactivated than the larger sizes, indicating that the reactivation process probably is diffusion controlled.

Similar conclusions are drawn from the data of Runs 17 and 18 with an 8 x 10 RCPP acceptor and the same stone ground to -200 mesh, and from Runs 19-21 where dead burned dolomite, ground to -270 mesh, was actually recarbonated to a higher degree than the equilibrium recarbonation ratio of RCPP acceptor. These experiments indicate that a large increase in surface area can be obtained by physically grinding spent dolomite; a fact which was confirmed by surface area measurements which show an increase of from 0.3 m^2/g to 1.4 m^2/g going from 28 x 65 mesh to -270 mesh.

Figure 5-31. ACCEPTOR ACTIVITY INCREASE VS. P_{H_2O}
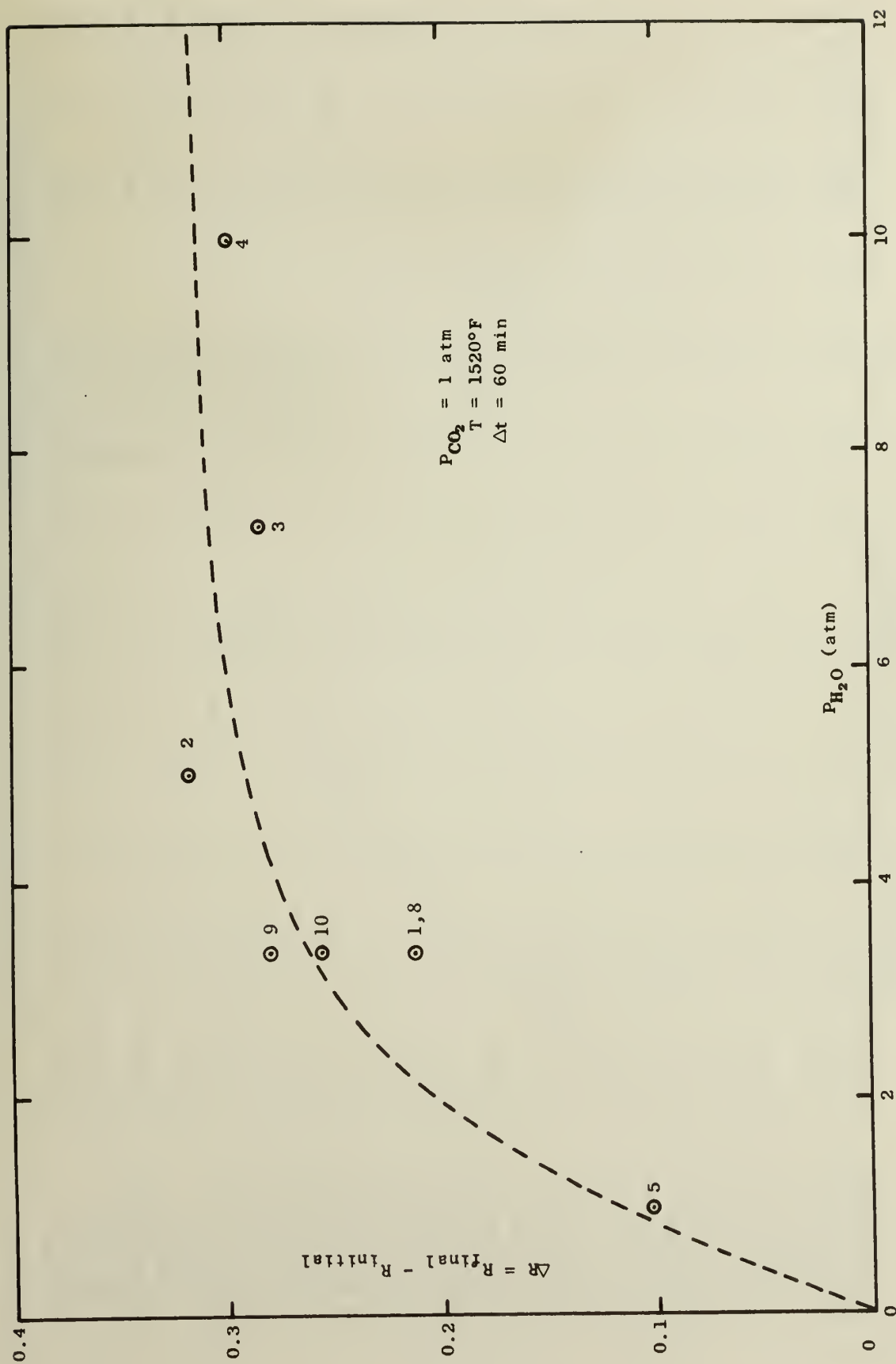
Table 5-40. SUMMARY OF CONTINUOUS CYCLE TESTER RUNS

| Run No.	Sample Information	Psig (Atm)	Regenerator			Gasifier						Cycle Time, min	No. of Cycles	$R_{Initial}$*	R_{Final}*	ΔR
			P_{CO_2} Atm	P_{N_2} Atm	Temp., °F	P_{CO} Atm	P_{H_2} Atm	P_{H_2O} Atm	P_{CO_2} Atm	P_{N_2} Atm	Temp., °F					
1	4476 Acceptor, Run 19 8 x 10 mesh	51.5 (4.5)	0.87	3.63	1840	0.0	0.0	3.48	1.02	0.0	1520	120	1	0.322	0.537	.215
2	4476 Acceptor, Run 19 8 x 10 mesh	73.5 (6.0)	1.16	4.84		0.0	0.0	5.03	0.97	0.0		120	1	0.240	0.557	.317
3	4476 Acceptor, Run 19 8 x 10 mesh	110.2 (8.5)	1.64	6.86		0.0	0.0	7.25	1.25	0.0		120	1	0.244	0.529	.285
4	4476 Acceptor, Run 19 8 x 10 mesh	147 (11.0)	2.12	8.88		0.0	0.0	10.01	1.00	0.0		120	1	0.253	0.552	.299
5	4476 Acceptor, Run 19 8 x 10 mesh	15 (2.0)	0.39	1.63		0.0	0.0	1.07	0.94	0.0		120	1	0.217	0.320	.103
6	3911 "old", Run 18 8 x 10 mesh	44.1 (4.0)	0.77	3.23		0.0	0.0	2.88	1.12	0.0		60	1	0.100	0.157	.057
7	3911 "old", Run 18 8 x 10 mesh	44.1 (4.0)	0.77	3.23		0.0	0.0	3.58	0.43	0.0		60	1	0.062	0.160	.098
8	4476 Acceptor, Run 19 8 x 10 mesh	66.2 (5.5)	1.06	4.44		0.0	0.0	3.46	1.02	1.02		120	1	0.307	0.522	.215
9	4476 Acceptor, Run 19 8 x 10 mesh	80.8 (6.5)	1.26	5.24		0.46	1.44	3.56	1.05	0.0		120	1	0.244	0.516	.272
10	4476 Acceptor, Run 19 8 x 10 mesh	95.5 (7.5)	1.45	6.05		0.42	1.34	3.35	0.98	1.40		120	1	0.242	0.497	.255
11	4476 "old", Run 19 8 x 10 mesh	51.5 (4.5)	0.87	3.63		0.0	0.0	3.51	1.00	0.0		120	1	0.114	0.306	.192
12	4476 "old", Run 19 65 x 100 mesh	51.5 (4.5)	0.87	3.63		0.0	0.0	3.50	1.00	0.0		120	1	0.095	0.243	.148
13	4476 "old", Run 19 100 x 150 mesh	51.5 (4.5)	0.87	3.63		0.0	0.0	3.53	0.97	0.0		120	1	0.143	0.391	.248
14	4476 "old", Run 19 150 x 200 mesh	51.5 (4.5)	0.87	3.63		0.0	0.0	3.61	0.89	0.0		120	1	0.160	0.453	.293
15	4476 "old", Run 19 200 x 270 mesh	51.5 (4.5)	0.87	3.63		0.0	0.0	3.50	1.00	0.0		120	1	0.210	0.535	.325
16	4476 "old", Run 19 -270 mesh	51.5 (4.5)	0.87	3.36		0.0	0.0	3.53	0.97	0.0		120	1	0.230	0.601	.371
17	3911 "old", Run 18 8 x 10 mesh	150 (11.2)	2.16	9.04		0.87	5.12	3.37	0.56	1.29		60	1	0.137	0.179	.042
18	Same as above ~ -200 mesh	150 (11.2)	2.16	9.04		0.86	5.10	3.43	0.55	1.28		60	1	0.179	0.333	.154
19	Dead Burned Dolomite 28 x 65 mesh	150 (11.2)	2.16	9.04		0.83	5.01	3.56	0.56	1.26		60	1	0.002	0.022	.020
20	Same as above -270 mesh	150 (11.2)	2.16	9.04		0.94	5.29	3.10	0.53	1.33		60	1	0.002	0.356	.354
21	Same as above -270 mesh	150 (11.2)	2.16	9.04		0.95	5.31	3.08	0.53	1.34		60	5	0.002	0.325	.323

* On Ca basis.

176
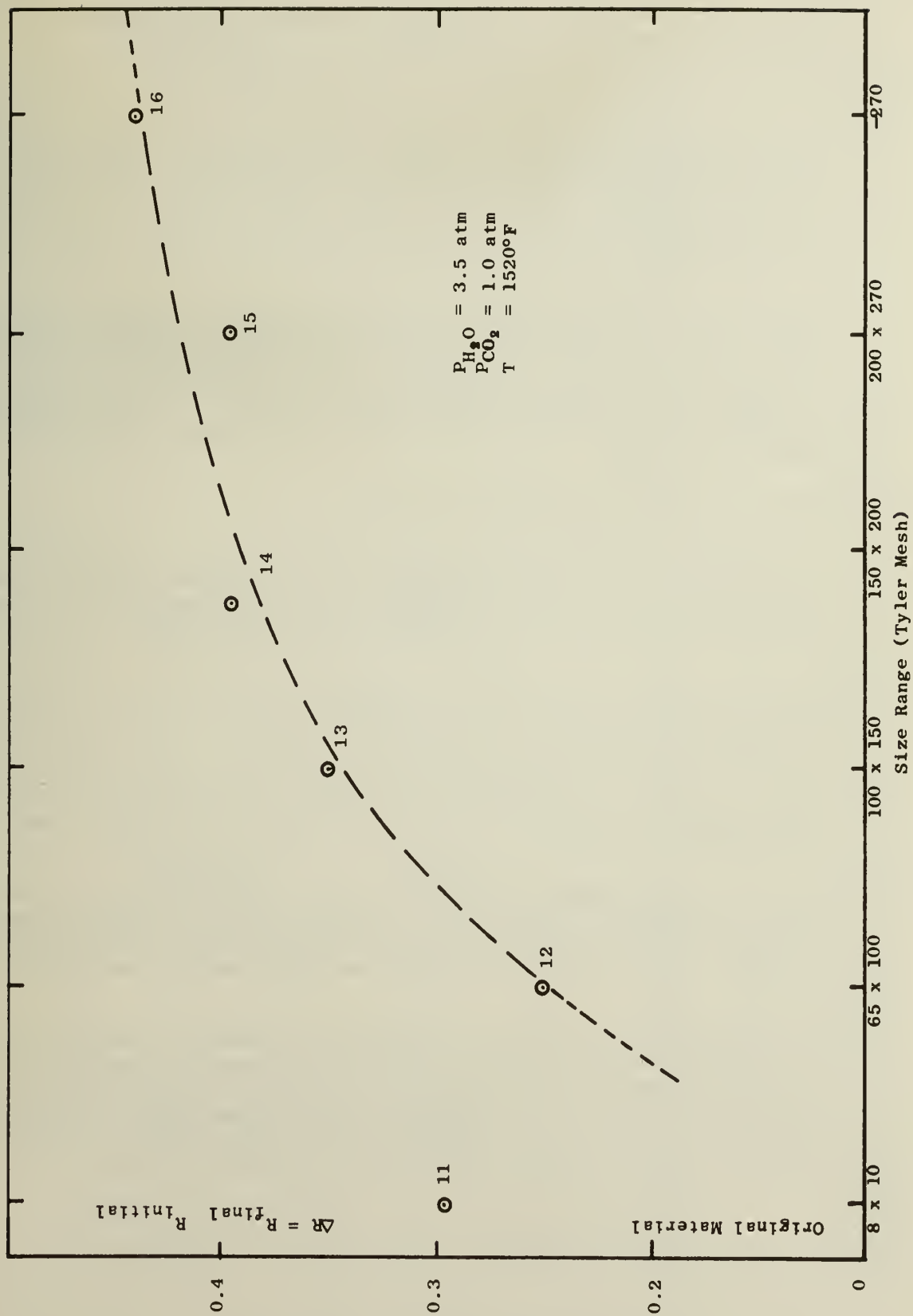
Figure 5-32. ACCEPTOR ACTIVITY INCREASE VS. SIZE

Also, the reactivation of dead-burned dolomite is not transitory, as indicated by sustained activity after five cycles (Run 21).

5.5.4.4.4 Effect of Bed Residence Times on Activity Patterns

The procedures for making cyclic runs in the automatic cycle tester have been described earlier in this report. Approximately 1 gram of the acceptor being examined was loaded into the unit via the sample holder assembly and the run was begun. All activity assays, except the final one for each run, were carried out in situ. The final assay for each run was done in the thermobalance.

The composition of the feed gas for the regeneration and gasification parts of the cycle was kept as constant as possible for this series of runs, and closely approximate the gas compositions in the vessels at the pilot plant. All runs reported here were made with a gasifier temperature of 1520°F and a regenerator temperature of 1840°F. The only significant differences between run conditions were the residence times in the different parts of the cycle.

5.5.4.4.5 Effect of Regenerator Residence Times

The gasifier residence time for each run in this series of experiments was held constant at 30 minutes, which was the nominal residence time in the gasifier and boot at the Rapid City Pilot Plant. Runs were made using both Tymochtee No. 11 dolomite and Rapid City limestone at both 50 minutes regeneration time and 10 minutes regeneration time per cycle.

For all runs made with 10-minute regeneration times, the flow rate of the calcination gas mixture was tripled to ensure an adequate flushing of carbonation gas prior to calcination. Runs No. 1 and 2, Table 5-41, give the data from the experiments on Tymochtee No. 11 dolomite, and Runs 6 and 7, Table 5-41, are the same experiments using Rapid City limestone as the acceptor. The activities shown in Table 5-41 are the Ca basis recarbonation ratios.

A cycle-by-cycle comparison of the activity data given in Runs 1 and 2 show a consistently higher acceptor activity in Run 2, where the regenerator residence time is five-fold shorter. This difference is even more apparent in Figure 5-33, which shows a comparison of the activity patterns for the two runs.

The magnitude of the effect of reducing the regenerator residence time in the pilot plant can perhaps best be demonstrated by a comparison of equilibrium activity obtained for a given make-up rate of fresh acceptor. The method for calculating equilibrium activity was described earlier in Subsection 5.5.4.1.2. The equations obtained from the data to represent the activity of a dolomitic acceptor at any given cycle are:

$$R = 0.77 \ N^{-0.2266} \qquad \text{for } N = 1 \text{ to } 19 \text{ cycles}$$

$$\text{and} \quad R = 2.25 \ N^{-0.5888} \qquad \text{for } N > 19 \text{ cycles}$$

Run No.	Sample	Cycle[*] Time (min)	No. of Cycles	Activity[**] (R)
1	Tymochtee No. 11 Dolomite 10 x 14 M	80 (50/30)	1	0.765
			15	0.409
			18	0.398
			30	0.313
			32	0.393
			44	0.262
			47	0.236
			62	0.201
			91	0.104
			94	0.142
			106	0.137
			109	0.114
2	Tymochtee No. 11 Dolomite 10 x 14 M	40 (10/30)	1	0.787
			5	0.644
			22	0.472
			28	0.485
			54	0.288
			107	0.242
			113	0.255
			135	0.329
			141	0.231
3	Tymochtee No. 11 Dolomite 10 x 14 M	60 (10/50)	1	0.947
			2	0.820
			17	0.834
			21	0.827
			36	0.629
			40	0.553
			55	0.367
			58	0.338
			73	0.254
			77	0.272
4	Tymochtee No. 11 Dolomite 10 x 14 M	60 (10/50)	1	0.838
			2	0.783
			18	0.755
			21	0.766
			37	0.518
			40	0.414
			55	0.315
			59	0.249
			61	0.308
5	Rapid City Limestone 20 x 28 M	80 (50/30)	1	0.732
			2	0.409
			13	0.174
			16	0.160
			28	0.156
			31	0.186
			42	0.091
			45	0.161

Table 5-41.   ACCEPTOR ACTIVITY DATA

Run No.	Sample	Cycle[*] Time (min)	No. of Cycles	Activity[**] (R)
6	Rapid City Limestone 20 x 28 M	40 (10/30)	1	0.685
			4	0.355
			26	0.159
			31	0.178
			45	0.119
			68	0.124
			73	0.088
			94	0.084
			99	0.055
7	Rapid City Limestone 20 x 28 M	80 (50/30)	1	0.425
			2	0.313
			14	0.236

[*] The first number under cycle time is the total time for a cycle; the numbers in parentheses are the regenerator and gasifier residence times, respectively.

[**] Activities on Calcium Basis - see text.

Note:

The following conditions were characteristic of all Runs:

Total P = 150 psig = 11.2 Atm

	Gasifier	Regenerator
P_{CO_2} (Atm)	0.70	2.45
P_{N_2} (Atm)	1.36	8.75
P_{H_2} (Atm)	4.65	--
P_{H_2O} (Atm)	3.50	--
P_{CO} (Atm)	0.99	--
T (°F)	1520	1840

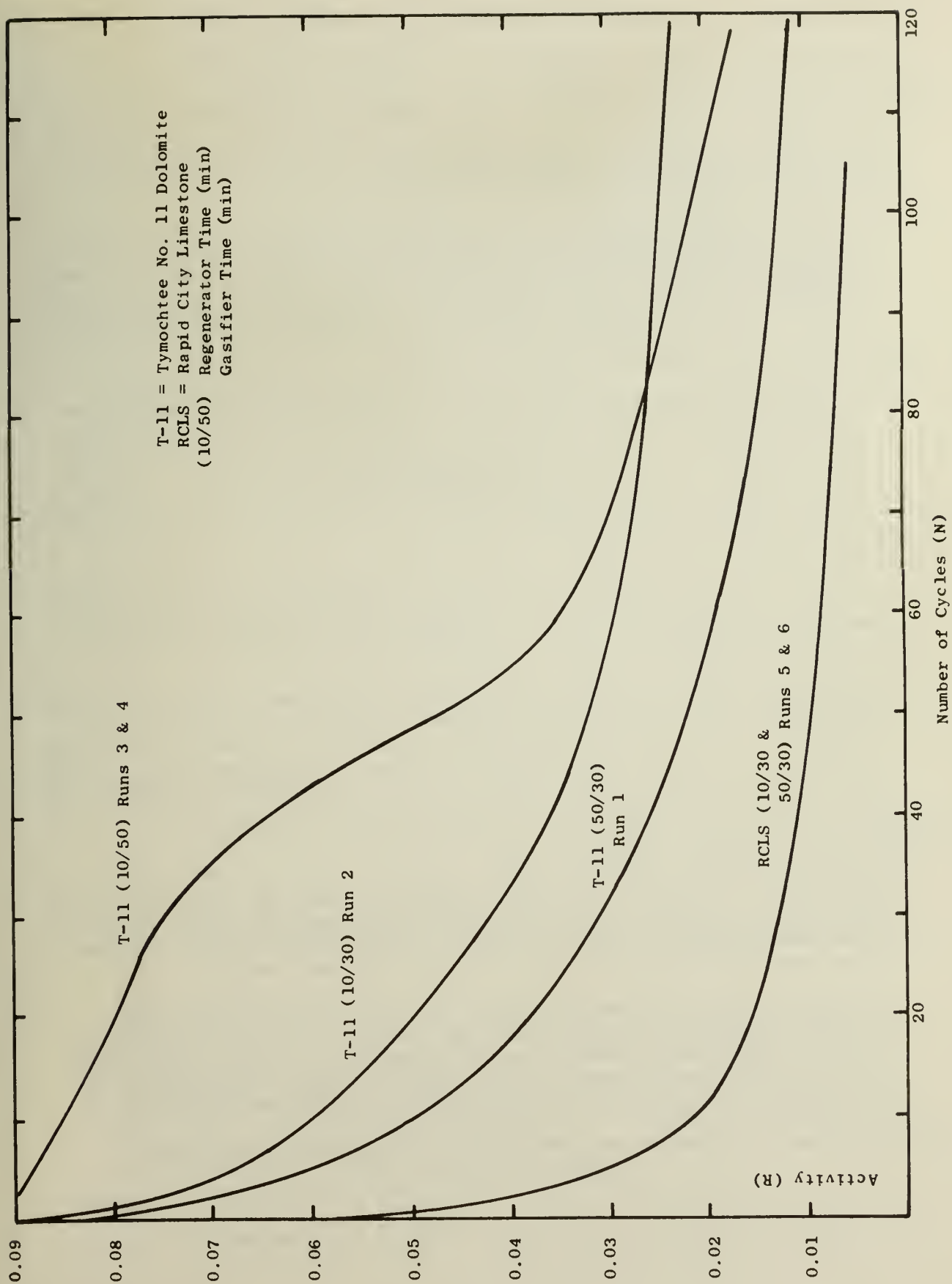Table 5-41.   ACCEPTOR ACTIVITY DATA (continued)

Figure 5-33. ACTIVITY PATTERN OF VARIOUS ACCEPTORS AT DIFFERENT CYCLE TIMES

181

for 50-minute regeneration time and 30-minute gasifier time, and

$$R = 0.79 \ N^{-0.1195} \qquad \text{for } N = 1 \text{ to } 17 \text{ cycles}$$

$$\text{and} \quad R = 1.89 \ N^{-0.4266} \qquad \text{for } N > 17 \text{ cycles}$$

for 10-minute regenerator time and 30-minute gasifier time, where R is the activity and N is the number of cycles.

Table 5-42 shows a comparison of the expected equilibrium activity for each of the above conditions at various make-up rates between 0.25 and 3%. These data indicate that only about 35 to 40% as much fresh stone is needed to maintain the same equilibrium activity when a retention time of 10 minutes is used in regeneration as opposed to 50 minutes. Such a reduction in make-up requirements would represent a significant savings in the operating costs of a CO_2 acceptor gasification plant.

Runs 5 and 6 (Table 5-41) were carried out using Rapid City limestone as the CO_2 acceptor. These runs were made with cycle times of 50-minute regeneration/30-minute recarbonation and 10-minute regeneration/30-minute recarbonation, respectively. A cycle-by-cycle comparison of activity of the two runs shows little or no difference between the activity pattern of the two runs, and their combined data yield the single curve for the limestone shown in Figure 5-33.

The activity of the limestone acceptor is considerably lower than that of dolomite-derived acceptor. This is especially true for a comparison such as the one in Figure 5-33, which is based on the molar ratio of CO_2 absorbed to Ca present.

Perhaps the more realistic way to compare limestone and dolomite activities is to base the activities on the ratio of CO_2 absorbed to the weight of acceptor. On this basis, the limestone gains about a factor of 2 over the dolomite, because of its much higher Ca content. When compared in this way, the limestone activity moves closer to that of the dolomitic acceptor; however, it is still slightly lower than that of the dolomite runs.

5.5.4.4.6 Effect of Gasifier Residence Times

Runs 3 and 4, Table 5-41, were made in order to test the effect of gasifier residence time on acceptor activity. In these runs, the regeneration cycle time was held constant at 10 minutes and the gasifier residence time was increased to 50 minutes from the 30 minutes of Runs 1 and 2.

The activity pattern demonstrated by these runs, Figure 5-33 is quite different from either that of Runs 1 or 2 above,. Here the activity shows a slow decline out to about 40 cycles, followed by a rapid activity loss similar to the initial few cycles of the other runs. The reason for this trend remains a mystery and will not be discussed further herein.

The best fit equations for these data, as explained earlier, are:

$$R = 0.94 \ N^{-0.0735} \qquad \text{for } N \leq 31 \text{ cycles}$$

$$\text{and} \quad R = 41.0934 \ N^{-1.1733} \qquad \text{for } N > 31 \text{ cycles}$$

which clearly show the steep drop in activity in the later stages of the run. As might be expected from a comparison of the data from Runs 3 and 4 with that of Runs 1 and 2, the equilibrium activity at a given fresh stone make-up rate is quite different for the (10/50) run versus the (10/30) runs. In Table 5-42 we see that at both 1/4% and 1/2% acceptor make-up rates the (10/30) cycle equilibrium activity is slightly higher than for the longer gasifier residence time runs. However, at higher make-up rates the (10/50) cycle yields significantly higher equilibrium activities. The reason for this lies in the fact that the lower the make-up rate the longer the average life of acceptor in the inventory. Thus, at low make-up rates the average "age" of acceptor is such that it is ≥ 80 cycles, beyond which point the (10/30) cycle stone has a higher activity than the (10/50) acceptor (Figure 5-33).

Table 5-43 presents the output from the equilibrium activity computer program for both the limestone and dolomite-derived acceptors, based on the calcined weight of acceptor. More explicitly, these activities are:

$$R = \frac{\text{Weight } CO_2 \text{ absorbed}}{\text{Calcined weight acceptor}}$$

From the data in Table 5-43, we see that the acceptor activity for limestone is slightly lower than that of Tymochtee dolomite for any given make-up rate at approximate Rapid City pilot plant conditions.

Finally, it should again be pointed out that remarkable agreement was obtained between the equilibrium activity data predicted by the laboratory cycle tester and the actual acceptor activities observed during the pilot plant runs in Rapid City. This is important, as it allows for rapid, accurate acceptor activity predictions to be made without the expense of actual plant operation.

5.5.5   SYNTHETIC ACCEPTORS

All of the experience with natural stone acceptors has indicated that make-up rates of fresh acceptor in excess of 1% will be required for the process to operate with no air being fed to the gasifier. This will lead to a significant expense for fresh acceptor make-up material in a commercial plant. It would be highly desirable to have an acceptor material with a much longer useful lifetime in plant operation. A rather large laboratory effort was made to create such a high activity, long-lived acceptor.

The object was to create an acceptor with the active calcium held in an inert matrix in such a manner as to permit process operation under $CaCO_3$-$Ca(OH)_2$-CaO melt-forming conditions. Operation under the melt-forming condition would permit nearly complete recarbonation during each pass through the gasifier and lead to a situation whereby the acceptor make-up rate would be determined by the attrition rate rather than activity decay. This would lower the fresh acceptor make-up requirement to something probably less than 0.1% and lower the costs accordingly.

	Make-up Rate				
Cycle Time	1/4%	1/2%	1%	2%	3%
(50/30)*	0.125	0.160	0.217	0.295	0.351
(10/30)	0.229	0.270	0.338	0.424	0.483
(10/50)	0.167	0.251	0.384	0.549	0.652

* (Min Regenerator/Min Gasifier)

Table 5-42.   TYMOCHTEE NO. 11 DOLOMITE EQUILIBRIUM ACTIVITY
(Ca BASIS)

Acceptor	Cycle Time	Make-up Rate				
		1/4%	1/2%	1%	2%	3%
Tymochtee No. 11 Dolomite	10/30*	0.089	0.105	0.132	0.165	0.188
Tymochtee No. 11 Dolomite	10/50	0.065	0.097	0.149	0.214	0.254
Tymochtee No. 11 Dolomite	50/30	0.049	0.062	0.084	0.115	0.137
Rapid City Limestone	10/30 50/30	0.060	0.065	0.075	0.088	0.099

* (Min Regenerator/Min Gasifier)

Table 5-43.   EQUILIBRIUM ACTIVITY OF VARIOUS ACCEPTORS
(CALCINED WT BASIS)

An attempt was made to infuse active calcium into a premanufactured inert matrix. This consisted of preparing a matrix by pressing finely divided (-325 M) periclase (MgO) powder into thin ($\sim$ 1-2 mm thickness) discs and sintering these discs in a Glo-bar furnace at $\sim$1500°C. This produced a rather porous chemically inert matrix which was physically quite durable. However, several attempts to fill the pore space with active calcium were unsuccessful. Only minor quantities of active calcium could be injected into the matrix and hence the idea was discarded.

A successful synthetic acceptor was synthesized in the following manner: Finely divided (70Å) silicon dioxide (Cab-o-Sil EB-5) was mixed with an excess of calcium carbonate (precipitated chalk), pelletized at 5,000 psig, and reacted at 1600°F (871°C) in 1 atm CO_2 (to prevent the calcination of $CaCO_3$) to form calcium mono silicate ($CaSiO_3$). This increases the particle hardness and permits further handling without particle degradation. When this material ($CaSiO_3$ with excess $CaCO_3$) is subjected to gasifier conditions with a high enough steam partial pressure to insure melt formation ($\geq$ 13 atm), the calcium silicate reacts with some of the remaining calcium carbonate to form spurrite ($Ca_5(SiO_4)_2CO_3$). This results in an acceptor comprised of active calcium carbonate encased in an inert spurrite matrix.

Synthetic acceptors, prepared in the above manner and containing up to about 40% free calcium carbonate, have been successfully cycled under melt-forming conditions. These synthetic acceptors have been cycled for up to 130 cycles with little or no activity loss and no loss of particle identity. Microscopic examination of these cycled acceptors has revealed very little migration of the free calcium.

A potential problem with synthetic acceptors, which has yet to be explored, is the effect of coal ash on the active calcium in these acceptors. If ash-acceptor reactions occur to any great extent, the practicality of this material will be greatly reduced. However, barring the possibility of severe ash-acceptor interactions, synthetic acceptors may provide significant cost savings in a commercial CO_2 acceptor plant.

5.6   SYSTEM HEAT LOSSES

The isolated operation of the regenerator and the gasifier systems in Runs 30 and 31 provided an opportunity to determine the individual heat loss from each system. These data formed the basis for the heat loss values used in all heat and material balances. The isolated operation excluded the unmeasured fuel char to the regenerator and circulating acceptor streams from the calculations, thereby increasing the accuracy of the heat loss determinations.

In each run, auxiliary fuel char or coal feed was burned with air to provide heat to maintain a normal operation temperature in the fluidized beds. Details of the operating procedures are listed in the individual run reports published in Volume 8, Book 4 of this report.

5.6.1   REGENERATOR BALANCES

The calculated heat and material balances for the regenerator system, Run 30, are listed in Tables 5-44 through 5-46. The three balance periods of Run 30 were differentiated by a change in the preheat temperature of the acceptor lift line gas flow. The intent of changing this preheat

Basis: 1 hour
Datum: 60°F, liquid water

	SCF	Lbs	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char Feed(1)		325	97	2,700	3,613,900
Acceptor Lift Gas(3)	55,700	4,537	1395	1,582,700	
Moisture	212	10	1395	17,300	
Char Lift Gas(3)	7,600	617	750	106,000	
Moisture	29	1	750	1,900	
Ring Gas			830		
Recycle(3)	40,000	3,263		629,700	
Air(4)	32,900	2,505		484,500	
Moisture	246	12		16,600	
Purge Gas, Recycle(3)	1,100	90	60		
Subtotal		11,360		2,841,400	3,613,900
Heats of Reaction					
Heat of Combustion In - Heat of Combustion Out				3,149,300	
CaO + S = CaS + O .057 Mols at 196,540 Btu/Mol				11,200	
Total		11,360		6,001,900	
Output					
Recycle Gas(3)	104,400	8,504	1863	4,127,900	
Vent Gas(3)	33,300	2,712	1863	1,316,000	394,000
Steam	1,844	88	1863	173,600	
Overhead Solids(2)		61	1863	28,500	43,400
Sulfur in Gas(5)	46	6	1863	2,500	27,200
Bed Inventory Loss		-11	1863		
Subtotal		11,360		5,648,500	464,600
Heat Loss (By Difference)				353,400	
Total		11,360		6,001,900	

	CHAR FEED (1)	OVERHEAD SOLIDS (2)
H, Wt %, Dry	2.11	
C	73.24	5.03
N	.68	
O	8.15	
S	1.84	3.00
Ash, SO_3 free	13.98	91.97
Wt %, Moisture	2.49	

	(3)	GAS (4)	(5)
H_2, Mol %	0.15		
CO	3.54		
CO_2	18.12		
N_2	78.19	79.00	
O_2		21.00	
COS, PPM*			31
H_2S, PPM*			39
SO_2, PPM*			259

* Based on total wet gas.

Table 5-44. HEAT AND MATERIAL BALANCE - RUN 30 0000 HOURS
TO 1200 HOURS DEC. 2, 1973 REGENERATOR SYSTEM -
BALANCE NO. 1 SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

	SCF	Lbs	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char Feed(1)		388	98	3,400	4,314,400
Acceptor Lift Gas(3)	58,200	4,740	1050	1,196,300	
Moisture	222	11	1050	16,100	
Char Lift Gas(3)	8,000	649	750	111,600	
Moisture	30	1	750	2,000	
Ring Gas			830		
Recycle(3)	39,900	3,255		628,200	
Air(4)	39,100	2,979		576,200	
Moisture	270	13		18,400	
Purge Gas, Recycle(3)	1,100	90	60		
Subtotal		12,126		2,552,200	4,314,400
Heats of Reaction					
Heat of Combustion In - Heat of Combustion Out				3,757,700	
CaO + S = CaS + O .117 Mols at 196,540 Btu/Mol				23,000	
Total		12,126		6,332,900	
Output					
Recycle Gas(3)	107,200	8,731	1852	4,210,200	
Vent Gas(3)	39,600	3,227	1852	1,555,600	470,100
Steam	2,150	102	1852	201,600	
Overhead Solids(2)		77	1852	36,000	64,300
Sulfur in Gas(5)	38	5	1852	2,000	22,300
Bed Inventory Loss		-16	1852		
Subtotal		12,126		6,005,400	556,700
Heat Loss (By Difference)				327,500	
Total		12,126		6,332,900	

	CHAR FEED (1)	OVERHEAD SOLIDS (2)
H, Wt %, Dry	2.11	
C	73.24	5.88
N	.68	
O	8.15	
S	1.84	4.87
Ash, SO₃ free	13.98	89.25
Wt %, Moisture	2.49	

	(3)	GAS (4)	(5)
H_2, Mol %	0.16		
CO	3.53		
CO_2	18.15		
N_2	78.16	79.00	
O_2		21.00	
COS, PPM*			31
H_2S, PPM*			40
SO_2, PPM*			184

* Based on total wet gas.

Table 5-45.   HEAT AND MATERIAL BALANCE - RUN 30 0800 HOURS
DEC. 3 TO 0800 HOURS DEC. 5, 1973 REGENERATOR
SYSTEM - BALANCE NO. 2 SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

	SCF	Lbs	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char Feed(1)		428	79	1,800	4,759,100
Acceptor Lift Gas(3)	76,600	6,296	600	834,600	
Moisture	323	15	600	20,000	
Char Lift Gas(3)	8,400	688	750	117,900	
Moisture	35	2	750	2,300	
Ring Gas			830		
Recycle(3)	19,000	1,564		301,200	
Air(4)	46,000	3,501		677,200	
Moisture	163	8		11,000	
Purge Gas, Recycle(3)	1,100	90	60		
Subtotal		12,592		1,966,000	4,759,100
Heats of Reaction					
Heat of Combustion In - Heat of Combustion Out				4,533,400	
CaO + S = CaS + O .171 Mols at 196,540 Btu/Mol				33,500	
Total		12,592		6,532,900	
Output					
Recycle Gas(3)	105,100	8,634	1842	4,134,100	
Vent Gas(3)	45,900	3,771	1842	1,804,800	144,300
Steam	2,380	113	1842	222,800	
Overhead Solids(2)		124	1842	57,200	78,100
Sulfur in Gas(5)	26	4	1842	1,500	3,300
Bed Inventory Loss		-54	1842		
Subtotal		12,592		6,220,400	225,700
Heat Loss (By Difference)				312,500	
Total		12,592		6,532,900	

	CHAR FEED (1)	OVERHEAD SOLIDS (2)
H, Wt %, Dry	2.11	
C	73.24	4.43
N	.68	
O	8.15	
S	1.84	4.41
Ash, SO_3 free	13.98	91.16
Wt %, Moisture	2.49	

|	(3)	GAS (4)	(5)
H_2, Mol %	.04		
CO	.94		
CO_2	19.71		
N_2	79.31	79.00	
O_2		21.00	
COS, PPM*			30
H_2S, PPM*			45
SO_2, PPM*			95

* Based on total wet gas.

Table 5-46.   HEAT AND MATERIAL BALANCE - RUN 30 1600 HOURS
DEC. 5 TO 1600 HOURS DEC. 6, 1975 REGENERATOR
SYSTEM - BALANCE NO. 3 SYSTEM PRESSURE 150 PSIG

temperature was to provide a broader range of data on which to base the calculations. All calculation procedures are consistent with previously published heat and material balances for the CO_2 acceptor process. Applicable equilibrium correlations, heat capacities, and heats of reaction can be found in a previously published report[5]. The determination of the gaseous sulfur in the regenerator overhead was made by calculating the net difference between the inlet and outlet solids sulfur and apportioning the sulfur species according to Reactions 5-56 and 5-57.

$$CaS + CO_2 = CaO + COS \qquad\qquad (5-56)$$

where: $\ln K_{equil} = -20.7776 + .010626T - 1.9848 \times 10^{-6}T^2 - 1611/T$

$\qquad T = {}^{o}F$

$$CaO + H_2S = CaS + H_2O \qquad\qquad (5-57)$$
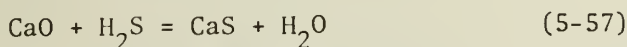
where: $\ln K_{equil} = 17.5646 - .0092926T + 1.7716 \times 10^{-6}T^2 - 1070/T$

$\qquad T = {}^{o}F$

The net remaining gaseous sulfur was assumed to be in the form of SO_2.

5.6.2 GASIFIER BALANCES

The gasifier heat and material balances for three of the balance periods of Run 31 are listed in Tables 5-47 through 5-49. Heat capacities and heats of reaction were again obtained from the previous reference[5]. For the purposes of these particular heat balances the net gaseous sulfur was assumed to be entirely H_2S. The amount of gaseous overhead sulfur was again determined by difference between the inlet and outlet solids streams.

Table 5-50 summarizes the results of the heat balances for Runs 30-31. It was necessary to include the heat loss from the lift line in the regenerator heat balances, because of the uncertainty of the gas temperature measurement at the top of the lift line. The listed heat losses for the regenerator lift line were calculated from skin temperature data collected during balance Period 2 of Run 30. Convection and radiation heat loss correlations[9] were used to determine the heat loss for this balance period. Since the operating conditions for this balance period more closely duplicated normal operating conditions, these results were used as the basis for the regenerator heat loss in all other heat and material balances. The lift line heat loss for the first and third balance periods was estimated by assuming the regenerator overall heat transfer coefficient, calculated from the results of Balance 2 to be constant over the range of bed temperatures, and calculating the lift line loss by difference. The convective and radiant method was preferred over the conductive calculation for the acceptor lift line, because portions of the original insulation between the inner pipe and the outer shell were removed and replaced with hand-packed Kaowool many times for repairs. Each time a hot spot developed on the outer shell during a run,

(5) Curran, G. P., et al, "Production of Clean Fuel Gas from Bituminous Coal," December, 1973, NTIS PB-232-695/AS. Work sponsored by EPA under Contract No. EX-76-C-01-1734.

(9) Chapman, A. J., "Heat Transfer." Second Edition, p. 526.

Basis: 1 hour
Datum: 60°F, liquid water

	SCF	Lbs	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Char Feed(1)		1,320	65	1,300	14,601,100
Boot Gas					
Recycle(5)	8,960	547	1385	264,200	
Steam	7,880	375	1490	639,700	
Ring Gas					
Air(6)	14,600	1,112	1490	417,100	
Steam	29,000	1,379	1490	2,434,500	
Purge Gas					
Recycle(5)	2,200	134	60		
Inert(7)	200	16	60		
Subtotal		4,883		3,756,800	14,601,100
Heats of Reaction					
CaO + CO₂ = CaCO₃	.88 Mols at 76,200 Btu/Mol			67,400	
Heat of Combustion In - Heat of Combustion Out				179,700	
Total		4,883		4,003,900	14,601,100
Output					
Vent Gas(5)	35,700	2,175	1340	1,018,600	6,457,200
Recycle Gas(5)	11,160	681	1340	316,700	
Steam	26,600	1,265	1340	2,128,500	
H₂S	181	16		5,800	115,600
Quench Tower Solids(2)		25	1340	10,300	203,100
Cyclone Solids(3)		210	1340	92,800	2,065,400
Purged Char(4)		511	1340	228,900	5,580,100
Subtotal		4,883		3,801,600	14,421,400
Heats of Reaction					
CaO + S = CaS + O	.25 Mols at 196,540 Btu/Mol			50,600	
Heat Loss				151,700	
Total		4,883		4,003,900	14,421,400

		LIGNITE OR CHAR						GAS	
	(1)	(2)	(3)	(4)			(5)	(6)	(7)
H, Wt %, Dry	2.11	.67	1.06	.93	CH₄, Mol %		5.33		
C	73.24	53.05	63.71	72.35	H₂		30.41		
N	.68	.36	.42	.35	CO		8.76		
O	8.15				CO₂		22.48		12.00
S	1.84				N₂		33.02	79.00	88.00
Ash					O₂			21.00	
Oxides	13.98	20.15	17.44	13.95					
CaCO₃		20.42	14.04	10.57					
CaS			5.35	3.33	1.85				
Wt %, Moisture	3.00								

Table 5-47. HEAT AND MATERIAL BALANCE - RUN 31-I 0400 HOURS
DEC. 14 TO 0800 HOURS DEC. 15, 1975 GASIFIER
SYSTEM HUSKY CHAR SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

	SCF	Lbs	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Coal Feed(1)		1,530	375	143,800	17,980,400
Boot Gas					
Recycle(5)	8,730	513	1415	255,800	
Steam	6,500	309	1415	532,800	
Ring Gas					
Air(6)	28,500	2,169	1503	829,700	
Steam	26,500	1,260	1503	2,242,300	
Purge Gas					
Recycle(5)	2,200	129	60		
Inert(7)	200	16	60		
Subtotal		5,926		4,004,400	17,980,400
Heats of Reaction					
$CaO + CO_2 = CaCO_3$ .33 Mols at 76,200 Btu/Mol				25,200	
Heat of Combustion In - Heat of Combustion Out				315,400	
Total		5,926		4,345,000	
Output					
Vent Gas(5)	68,300	4,020	1470	2,094,400	14,023,400
Steam	18,400	875	1470	1,536,200	
Recycle Gas(5)	10,900	642	1470	334,700	
H_2S	89.8	8	1470	3,200	57,400
Quench Tower Solids(2)		52	1470	24,900	497,400
Cyclone Solids(3)		185	1470	92,100	1,932,100
Purged Char(4)		144	1470	66,000	1,154,700
Subtotal		5,926		4,151,500	17,665,000
Heats of Reaction					
$CaO + S = CaS + O$ .12 Mols at 196,540 Btu/Mol				23,600	
Heat Loss				169,900	
Total		5,926		4,345,000	

		COAL OR CHAR					GAS	
	(1)	(2)	(3)	(4)		(5)	(6)	(7)
H, Wt %, Dry	4.55	.62	.85	.52	CH_4, Mol %	5.56		
C	69.49	63.90	69.03	53.45	H_2	28.55		
N	.91	.40	.40	.25	CO	17.55		
O	16.27				CO_2	14.87		12.00
S	.75				N_2	33.47	79.00	88.00
Ash					O_2		21.00	
Oxides	8.03	19.84	19.85	35.05				
$CaCO_3$		12.12	8.40	7.69				
CaS		3.12	1.47	3.04				

Table 5-48.   HEAT AND MATERIAL BALANCE - RUN 31-II 0000 HOURS
TO 2400 HOURS DEC. 22, 1975 GASIFIER SYSTEM
WESTMORELAND SARPY CREEK SUBBITUMINOUS COAL
SYSTEM PRESSURE 150 PSIG

Basis: 1 hour
Datum: 60°F, liquid water

	SCF	Lbs	°F	Sensible Heat BTU	Heat of Combustion BTU
Input					
Coal Feed(1)		1,470	375	138,200	17,297,300
Boot Gas					
Recycle(5)	9,400	556	1411	273,900	
Steam	6,500	309	1411	532,100	
Ring Gas					
Air(6)	29,300	2,231	1515	853,000	
Steam	26,400	1,255	1515	2,236,400	
Purge Gas					
Recycle(5)	2,200	130	60		
Inert(7)	200	16	60		
Subtotal		5,967		4,033,600	17,297,300
Heats of Reaction					
CaO + CO₂ = CaCO₃ .251 Mols at 76,200 Btu/Mol				19,100	
Heat of Combustion In - Heat of Combustion Out				380,000	
Total		5,967		4,432,700	
Output					
Vent Gas(5)	68,000	4,014	1480	2,095,500	13,553,500
Steam	19,500	926	1480	1,630,100	
Recycle Gas(5)	11,600	686	1480	357,100	
H₂S	93.6	8	1480	3,400	59,800
Quench Tower Solids(2)		44	1480	21,100	410,300
Cyclone Solids(3)		153	1480	77,300	1,617,100
Purged Char(4)		136	1480	65,100	1,276,600
Subtotal		5,967		4,249,600	16,917,300
Heats of Reaction					
CaO + S = CaS + O .065 Mols at 196,540 Btu/Mol				12,700	
Heat Loss				170,400	
Total		5,967		4,432,700	

		COAL OR CHAR					GAS		
	(1)	(2)	(3)	(4)		(5)	(6)	(7)	
H, Wt %, Dry	4.88	.59	.88	.58	CH₄, Mol %	5.21			
C	69.35	62.38	69.80	62.98	H₂	28.42			
N	.95	.38	.44	.29	CO	16.93			
O	17.52				CO₂	14.88		12.00	
S	.68				N₂	34.56	79.00	88.00	
Ash					O₂		21.00		
Oxides	6.62	24.88	18.85	29.34					
CaCO₃		9.16	9.04	5.32					
CaS		2.61	.99	1.49					

Table 5-49.   HEAT AND MATERIAL BALANCE - RUN 31-III
             0600 HOURS DEC. 27 TO 0800 HOURS DEC. 28, 1975
             GASIFIER SYSTEM WYODAK SUBBITUMINOUS COAL
             SYSTEM PRESSURE 150 PSIG

Regenerator Heat and Material Balances
Run 30

	Balance 1	Balance 2	Balance 3
Average Bed Temperature, °F	1863	1852	1842
Total Heat Loss,* Btu/hr	353,400	327,500	312,500
Heat lost by Acceptor Lift Line, Btu/hr	80,500	56,200	42,700
Net Heat lost by Regenerator Vessel Only, Btu/hr	272,900	271,300	269,800

* Includes the acceptor lift line, CD-208.

Gasifier Heat and Material Balances
Run 31

	Balance 1	Balance 2	Balance 3
Feed	Husky Char	Sarpy Creek Subbituminous Coal	Wyodak Subbituminous Coal
Bed Temperature, °F	1340	1470	1480
Heat lost by Gasifier Vessel, Btu/hr	151,700	169,900	170,400

Table 5-50. SUMMARY OF REGENERATOR AND GASIFIER HEAT AND MATERIAL BALANCES RUNS 30 AND 31

the area of the hot spot had to be cut open. The vacuum-formed Kaowool insulation was removed to make the repairs, then the annular space in the area of the repair was hand packed with bulk Kaowool. These many repaired areas made the determination of the lift line heat loss impossible using thermal resistance-type correlations, because of the unknown K factor for the insulation.

5.6.3   HEAT LOSS FROM REGENERATOR REFRACTORY LIFT LINE

The radiation and convection method[9] was used to estimate the heat loss of the refractory lift line which replaced the original regenerator lift line after Run 40. Thermal resistance correlations were used to estimate the heat loss of all other transfer lines in which the insulation quality was known with reasonable certainty. Sample calculations using both types of calculation procedures to estimate the heat loss of the refractory lined lift line are listed in Subsection 5.6.5. Skin temperature data collected during Run 41B are listed in Table 5-51. The skin temperature used in the calculations represents a weighted mean temperature, based on the average temperature of the line on each floor of the pilot plant structure and the length of line exposed on each floor. The difference in the calculated heat loss obtained by the two methods in the sample calculations is possibly the result of inaccurate temperature measurements. For this particular line, a mean value of the two calculations was used (120,800 btu/hr).

5.6.4   SUMMARIZED HEAT LOSSES

A summary of the gasifier and regenerator system heat losses as used in the integrated plant heat and material balances is listed in Table 5-52. These heat loss values reflect the modifications that were made to the plant during the operating period.

5.6.5   SAMPLE CALCULATIONS

Heat Loss from Refractory Lined Acceptor Lift Line CD-208.

(1) Heat conduction

Heat flow in cylinder, composite wall:

$$q = \frac{t_1 - t_n}{\dfrac{D_n}{2K_1} \ln \dfrac{D_1}{D} + \dfrac{D_n}{2K_2} \ln \dfrac{D_2}{D_1} + \ldots + \dfrac{D_n}{2K_n} \ln \dfrac{D_n}{D(n-1)}}$$

$K = Btu/ft^2 \ hr \ {}^\circ F/in.$

$q = Btu/ft^2 \ hr$

$t_1 = $ Hot face temperature, ${}^\circ F$

$t_n = $ Cold face temperature, ${}^\circ F$

$D = $ Inside diameter of cylinder, inches

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(9) Chapman, A. J., "Heat Transfer." Second Edition, p.526.

Date			12/27/76				12/28/76				
Time			1200	1700	2000	2400	0400	0800	1200	1600	2000
Floor	Elevation ft.										
6	84.2		260	280	300	310	310	300	270	250	240
6			280	280	200	220	240	260	260	250	240
5	68.2		240	240	240	235	330	230	220	250	250
5	*		440	490	480	470	280	420	420	400	420
4	54.2		220	210	220	230	235	220	230	230	230
4			260	240	240	260	250	250	230	210	210
3	40.2		230	230	250	260	240	230	220	210	210
3			220	230	220	230	220	210	220	210	210
1	4.2		240	255	220	220	225	225	220	200	200
1	0		250	240	250	245	250	250	260	240	240

* Localized hot spot.

All temperatures are in °F

Table 5-51. SKIN TEMPERATURES, ACCEPTOR LIFT LINE, CD-208

	Runs 21-28B	Runs 29A-32	Runs 33-40	Run 41	Runs 42-47B
Regenerator	271.3[1]	271.3	271.3	271.3	257.9[4]
Acceptor Lift Line	80.5	80.5	80.5	120.8[3]	120.8
Engager Pot	11.0	11.0	11.0	11.0	11.0
Recarbonated Acceptor Standleg	9.8	18.1	18.1	18.1	18.1
Char Lift Line	5.5	5.5	5.5	5.5	5.5
Char Standleg	26.9	26.9	28.0	26.9	26.9
Regenerator System Total	405.0	413.3	414.4	453.6	440.2
Gasifier	170.0[2]	170.0	170.0	170.0	170.0
Calcined Acceptor Standleg	28.0	28.0	28.0	28.0	28.0
Gasifier System Total	198.0	198.0	198.0	198.0	198.0

(1) Run 30 results used, Balance No. 2 (see Table 5-50).
(2) Run 31 results used, (see Table 5-50).
(3) Lift line was lined with refractory; heat loss calculated.
(4) Regenerator diameter reduced; reduction in heat loss calculated from thermal properties of refractory.

Table 5-52. SUMMARY OF HEAT LOSSES

196

D_1 = Outside diameter of inside lining material, inches

D_2 = Outside diameter of secondary lining material, inches

D_n = Outside diameter of outer lining material, inches

K_1 = Thermal conductivity of inside lining material

K_2 = Thermal conductivity of secondary lining material

K_n = Thermal conductivity of outside lining material

A, = outside area of line, CD-208 = $\pi \dfrac{(10.75)}{12} (86.75)$ = 244.14 ft^2

Inside temperature, T_1 = 1390°F

Average outside skin temperature, T_2 = 238°F

D = 4 in.

D_1 = 8 in. K_1, Mulfrax = 17 at 1400-2000°F

D_2 = 10 in. K_2, Fiberfrax = .6 at 750°F

D_3 = 10.75 in. K_3, Carbon Steel Shell = 360

$$q = \frac{1390 - 238}{\dfrac{10.75}{2(17)}\ln\dfrac{8}{4} + \dfrac{10.75}{2(.6)}\ln\dfrac{10}{8} + \dfrac{10.75}{2(360)}\ln\dfrac{10.75}{10}}$$

$$q = \frac{1152}{(.219 + 1.999 + .001)}$$

q = 519.1 Btu/ft^{2}hr

Q = A x q = (244.14) (519.1) = 126,733 Btu/hr

(2) <u>Convection and Radiation</u>

For vertical cylinders:

$$h_c = N_{nul}\ \frac{K}{L}^{(9)}$$

$$h_r = \sigma\epsilon\ (T_s - T_a)(T_s^2 + T_a^2)\ ^{(9)}$$

$$Q = A (h_c + h_r)(\Delta T)$$

(9) Chapman, p. 525.
(9) Ibid, p. 313.

h_c = Convective heat transfer coefficient, Btu/hr ft^2 ^{o}F

h_r = Radiant heat transfer coefficient, Btu/hr ft^2 ^{o}F

Q = Heat transfer rate, Btu/hr

N_{nul} = Nusselt number, dimentionless

K = Thermal conductivity of air, Btu/hr ft ^{o}f

L = Vertical length of cylinder, ft

σ = Stephan-Boltzman constant, .17174 x 10^{-8} Btu/hr ft^2 ^{o}R^4

ϵ = Emissivity of radiating surface, painted steel = .9

T_s = Temperature of radiating surface, ^{o}R

T_a = Ambient air temperature, ^{o}R

T_s = 238°F, T_a = 60°F, L = 86.75 ft

Mean film temperature = $\dfrac{(238 + 60)}{2}$ = 149°F

Properties of air at 150°F

ρ, density = .06508 lb/ft^3

μ, viscosity = .04899 lb/ft hr

$'$K, Thermal conductivity = .01688 Btu/hr ft ^{o}F

N_{pr} Prandtl number, dimentionless = .699

β, Coefficient of thermal expansion, 1/^{o}R = .0019

g, Newton conversion factor = (32.2)(3600)^2

Grashof number $N_{Gr} = \dfrac{L^3 \rho^2 \beta g \Delta T}{\mu^2}$

$$N_{Gr} = \frac{(86.75)^3 (.06508)^2 (32.2)(3600)^2 (238-60)}{(520)(.04899)^2}$$

$$N_{Gr} = 1.65 \times 10^{14}$$

N_{nul} = .129 $(N_{Gr} \times N_{pr})^{1/3}$

N_{nul} = .129 $(1.65 \times 10^{14} \times .699)^{1/3}$

$$N_{nu1} = 6272.5$$

$$h_c = N_{nu1} \times \frac{K}{L}$$

$$h_c = \frac{(6272.5)(.01688)}{(86.75)} = 1.221 \text{ Btu/hr ft}^2 \, ^\circ F$$

$$h_r = .1714 \times 10^{-2} \times .9 \left(\frac{698}{100} + \frac{520}{100}\right) \left[\left(\frac{698}{100}\right)^2 + \left(\frac{520}{100}\right)^2\right]$$

$$h_r = 1.423 \text{ Btu/ft}^2 \text{ hr } ^\circ F$$

$$Q = (244.14)(1.221 + 1.423)(238-60)$$

$$Q = 114,900 \text{ Btu/hr}$$

5.7 BENCH-SCALE SUPPORT STUDIES

Systematic analyses and evaluations of samples of the various solids streams from balance periods in each pilot plant run were carried out in the laboratory in Library. Normally, this work was performed on samples selected and shipped to Library at the conclusion of a run; however, occasionally information was required during a run and various samples were analyzed or experiments conducted accordingly. Other support work carried out in Library consisted of the development and testing of synthetic acceptors, reactivation of spent acceptors, and acceptor reconstitution.

5.7.1 ROUTINE SAMPLE WORKUP

The routine sample treatment and assessment for each of the solids stream analyzed is described below. The information gathered from this work was used to define the progress of and changes which occurred during a run.

5.7.1.1 Gasifier Boot Samples

The recarbonated acceptor samples obtained from the gasifier boot, S-10, sampling port were the key samples for the determination of acceptor activity. These samples were processed in the following manner: Initially, the sample was riffled to one-half its original weight and a screen analysis was performed. The sample was screened at 6, 8, 10, 14, and 20 mesh (Tyler sizes) and at this stage any sample peculiarities were noted. These screen analyses provided a rapid means of evaluating such things as char-stone separation at the boot-gasifier interface and acceptor attrition.

The plus 20 mesh size fractions of these S-10 samples were assayed for acceptor activity as described below.

Approximately 10 grams of a given stone fraction was loaded into a previously tared quartz tube reactor (a 2.5 cm diam. x 30 cm long quartz tube, with one end sealed in the shape of a cone, and a 0.6 cm diam. dip tube extending to the bottom of the tube) and weighed. The reactor was purged by passing a stream of CO_2 gas through the sample via the

dip tube. After purging, the reactor, with CO_2 still flowing through it, was lowered into a sand bath furnace at 1000°F (538°C). The sample was maintained at these conditions for 15 minutes to ensure that any moisture present in the sample was driven off prior to the activity determination. Following this 15-minute drying, the reactor was quenched in a water bath, purged with N_2, and weighed again. Next, a stream of H_2 was passed through the sample and the reactor was heated to 1700°F (927°C) and fully calcined for 45 minutes. The reactor was then quenched, purged with N_2, and reweighed. Finally the sample was recarbonated by heating the quartz tube reactor to 1500°F (816°C) for 30 minutes in a stream of CO_2 gas. The final weight of the reactor plus sample in 1 atm of N_2 gas was recorded and the sample was saved.

The activity, R, of these samples was then calculated by dividing the calcination weight loss, W, by the calcined weight, C, multiplied by the appropriate gravimetric factor, F_2 for the stone involved (see 5.7.2.1):

$$R = \frac{W}{C \times F_2} \qquad (5\text{-}58)$$

The particle density of these S-10 stones was also routinely determined. For the density measurement, a small ($\sim$ 2-3 gm) sample of the stone was loaded into a pre-tared pyrex pycnometer of 5.910 cc volume and weighed. The pycnometer was then evacuated and warmed to drive off any absorbed surface moisture and reweighed. The remaining volume of the apparatus was filled with mercury and the pycnometer was reweighed. The particle density of the samples were then calculated by the following equation:

$$\rho = \frac{\text{Sample wt}}{\text{Vol of pycnometer} - \dfrac{\text{Wt of mercury}}{\text{Density of mercury}}} \qquad (5\text{-}59)$$

These particle densities were quite useful in determining the circulation characteristics of the acceptor, as well as such things as degree of acceptor-ash interaction (shell formation) and particle shrinkage.

Occasionally, the S-10 acceptor samples were chemically analyzed to determine their elemental composition. Knowledge of the chemical composition compared with the particle densities and acceptor activity was of great importance in the evaluation of the performance of the various coal-acceptor combinations employed during plant operations.

5.7.1.2 Feed Coal Samples

Samples of the ground feed coal as fed to the preheater (S-3 samples) and as fed from the preheater into the gasifier lockhopper (S-8 samples) were routinely examined. The samples normally were screened at 100 Tyler mesh and both the +100 and -100 M fractions were submitted to the analytical laboratory for determination of the moisture and ash contents as well as the abundance of carbon, hydrogen, nitrogen, and sulfur. Elemental analyses were obtained on the ash from these samples and the heating value of the coal was measured.

The data gathered on these feed coal samples provided a continuous check on the constancy and quality of the feed coal, as well as information on the performance of the grinding and drying sections of the pilot plant.

5.7.1.3   Gasifier Bed Material Samples

Samples of the gasifier bed material, S-13B, from the balance periods of each run were studied. These samples, consisting normally of circulating acceptor and partially gasified char, were riffled to about 300 grams and screened at 8, 10, 14, 20, 28, 35, 48, 65, 100, and 200 Tyler mesh. Next, the char and acceptor were separated in each size fraction and their weight percentages calculated. For the 10 x 14, 14 x 20, 20 x 28, and 28 x 35 mesh size fractions, the char-acceptor separation was carried out by elutriating the char from the stone in a pyrex column with a stream of nitrogen gas. After the elutriation step, the fractions were examined under a light microscope and further separation, if necessary, was done by hand picking.

Due to the extreme difficulty of elutriating or hand picking the smaller size fractions, another separation method was devised for these samples. For the 35 x 48 and 48 x 65 mesh samples, the weight fraction of stone and char was determined by ashing about 20 grams of sample in a muffle furnace in air followed by screening at 48 mesh, 65 and 100 mesh. The screening was performed by forcing all powder and loose aggregates through the screens with a gentle rotary action of the finger. The material on each screen, as well as that in the pan, was then weighed. The pan (-100 m) material was taken to be the inherent ash in the char and the +100 mesh material was considered to be intermediate fines or "junk."

The size fraction smaller than 65 mesh (i.e., 65 x 100, 100 x 200 and -200 M) were taken to be free of acceptor material and to consist entirely of coal fines.

The particle density of the S-13B char samples was measured directly, by the mercury density method outlined above for the S-10 samples, on all of the size fractions except the 35 x 48 and 48 x 65 mesh sizes. Whenever it was important to know the char density in these fractions, the densities were calculated in the following manner: The density of the bulk size fraction of material was measured in the previously described manner. Following this density measurement, the sample was completely removed from the pycnometer and ashed in a muffle furnace. The inherent ash and acceptor material were separated by the finger screening method described above for these size fractions. Finally, the density of the nonash material was measured via the mercury density method. With the above information, the particle density of the char could be calculated as follows:

$$\rho_{Char} = \frac{(1 - A)}{\frac{1}{B} - \frac{A}{C}} \qquad (5-60)$$

where: A = weight fraction nonash material, B = measured particle density of total sample, C = measured particle density of the nonash material.

201

In addition to the above described screen analyses, char-acceptor
separation, and char density determinations, S-13B char samples were
routinely selected and submitted to the analytical laboratory for
complete analysis as described for the S-3 and S-8 coal samples.

The information obtained from these gasifier bed samples was vital for
the calculation of the carbon inventory and of the acceptor retention
time.

5.7.1.4   Cyclone Material Samples

Samples of the overhead fines material from both the regenerator cyclone,
S-15A and S-15B, and from the gasifier external cyclone, S-17, were
routinely analyzed.

The regenerator overhead fines were normally riffled to one-half of the
original weight and screened as follows:

(1)   The S-15B samples (material from the first of the two cyclones
      in series) were screened at 8, 10, 14, 20, 28, 35, 48, 65, 100,
      200, and 325 Tyler mesh).
(2)   The S-15A samples (material from the second regenerator cyclone)
      were screened at 35, 48, 65, 100, 200 and 325 Tyler mesh.

Since the S-15A cyclone was downstream from the S-15B cyclone, it was
rare that any +35 mesh material was found in the S-15A samples; hence
the elimination of the larger screen sizes. Generally speaking, the
regenerator overhead material consisted of finely divided coal ash and
attrited fines from the acceptor. Very little unburned carbon was present
in these samples under normal operating conditions.

Solids from the gasifier external cyclone (S-17 samples) were usually
riffled in half and screened at 65, 100, 200, and 325 Tyler mesh.
Normally the -65 mesh material was recombined and submitted to the analy-
tical lab for ultimate analysis; however, occasionally the individual size
fractions were analyzed. Under ordinary operating conditions this material
was composed of ungasified char fines and attrited acceptor fines.

Characterization of these regenerator and gasifier overhead fines material
was beneficial in helping to gain knowledge of factors such as acceptor
attrition rates and carbon burn up efficiency in the regenerator.

5.7.2   OCCASIONALLY STUDIED SAMPLES

In addition to the routinely assayed samples, the following materials
were examined from time to time either as a check on the uniformity of
plant conditions among the various runs or when specific problems needed
attention.

5.7.2.1   Fresh Feed Acceptor Samples

Samples of the ground and sized fresh feed acceptor, S-6, were periodically
examined to ensure that no major changes in the properties of these materials
had occurred between runs. These stones were screened at 6, 8, 10, and

14 Tyler mesh as a check on the grinding system. The particle density of the S-6 stones was measured, by the method described above, on both fresh, as-received acceptor and stones which had been calcined at $1500^{\circ}F$ $(816^{\circ}C)$, as a check on acceptor uniformity. The gravimetric factor, F_2,[3] for these feed acceptors was determined in the following manner.

The sized sample, weighing about 25 grams, was placed in a quartz tube reactor which was heated by being immersed in a fluidized sand bath furnace. The reactor and its contents were weighed on an analytical balance after each of the following steps:

(1) The sample was heated in CO_2 at atmospheric pressure and at $1100^{\circ}F$ for 15 minutes. The weight loss represented the moisture content, hydrate water, the CO_2 content of unstable carbonates, one-half of the pyritic sulfur, and pyrolysis of the bitumen content. For all the acceptors used in the operating program, this weight loss was less than 0.5% of the raw stone.

(2) The sample then was exposed to 1 atm CO_2 partial pressure at $1550^{\circ}F$ for 30 minutes. The weight loss represented the CO_2 content of $MgCO_3$ and the CO_2 lost during reaction of some of the $CaCO_3$ with impurities, as discussed later.

(3) The sample then was calcined by heating in N_2 at $1600^{\circ}F$ for 30 minutes. The weight loss gave the desired useful CaO content, since the CO_2 loss was proportional to the useful $CaCO_3$ content of the stone.

(4) The sample then was recarbonated in 1 atm CO_2 at $1500^{\circ}F$ for 30 minutes. This was done to complete the calcining-recarbonation cycle. Characteristically, the dolomites showed a weigh gain of 95-97% of the weight loss on the previous calcining, and the limestones showed 66-68%.

Supplemental tests showed that all reactions were complete in the time intervals stated above.

Except for dolomites which had very low impurity contents, the weight loss on calcining the $MgCO_3$ was greater than that on calcining the $CaCO_3$. Since dolomites with a mol ratio of $MgCO_3/CaCO_3$ greater than the theoretical ratio of unity are a geological rarity, some of the $CaCO_3$ must have reacted with an impurity such as SiO_2 according to,

$$CaCO_3 + SiO_2 = CaO \cdot SiO_2 + CO_2$$
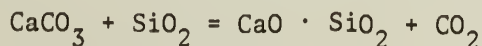
The gravimetric factor, F_2, [3] was defined as:

$$F_2 = \frac{CO_2 \text{ Wt loss in Step 3}}{\text{Calcined sample wt after Step 3}} \qquad (5-61)$$

This factor is a good parameter for the evaluation of acceptor constancy.

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(3) Interim Rpt. No. 3, Book 3, Phase II, "Bench-Scale Research on CSG Process - Operation of the Bench-Scale Continuous Gasification Unit," January, 1970. Research and Development Report No. 16, National Technical Information Service PB-184720/AS.

Another test which was performed occasionally on fresh acceptor feedstock was to determine the activity pattern by cycling the material under simulated pilot plant conditions in a continuous automatic cycle test unit. This cycle tester consisted of a 0.5 inch I.D. stainless steel tube with two independently controlled temperature zones. The sample was raised and lowered between the high-temperature calcination zone and the lower temperature recarbonation zone. A CO_2-N_2 gas mixture was passed through the reactor while the sample was in the calcination zone, to simulate the condition in the pilot plant regenerator. A CO_2-H_2-CO-N_2-H_2O mixture was normally employed in the recarbonation zone, to be consistent with conditions in the pilot plant gasifier. Normally a pressure of 11 atm absolute was maintained in the reactor, although various other pressures were employed from time to time. The results of this cycle tester work were in very good agreement with the actual plant data on acceptor activity and thus were quite beneficial in predicting plant performance on a given acceptor. This was especially true in the work done on reconstituted acceptor.

Occasionally the S-6 samples were sent to the analytical lab for chemical analysis. These analyses, coupled with the assay data, ensured that the acceptors obtained in different shipments and from different parts of a quarry were not substantially different in composition--especially calcium content.

5.7.2.2   Regenerator Samples

Acceptor samples from the regenerator return leg, S-9, and from the spent acceptor withdrawal hopper, S-18, were monitored for several key variables.

One important item checked was whether the stones had been completely calcined in the regenerator. This was determined by subjecting a several gram, previously dried sample of the acceptor to $1700°F$ ($927°C$) in a quartz tube reactor under 1 atm of nitrogen gas and measuring the weight loss, if any, which occurred. Only on very rare occasions were these samples found to contain residual CO_2. This fact confirmed that the regenerator was performing as designed.

The recarbonation activity and the particle densities of these calcined acceptors was also measured periodically, as was the elemental composition. These data, together with that obtained from the S-10 samples, further aided in the analysis of the performances of various acceptors.

5.7.2.3   Intermediate Fines

During the pilot plant runs, a problem arose with build-up of an inventory of intermediate sized (20 mesh x 65 mesh) fines in the gasifier-regenerator system. This buildup led to high gasifier bed densities, which in extreme cases hindered the showering of the acceptor through the gasifier char bed and necessitated the use of combustion air to supply the missing heat necessary for the gasification reaction.

Screen analyses of the coal ash, via the finger-screening technique explained earlier, showed that the ash of all the coals contained small-sized quartz grains. Microscopic examination of the intermediate fines material revealed that the majority of these particles contained a center core of SiO_2 (quartz) surrounded by a silica rich material of essentially the same composition as the coal ash. Apparently the intermediate fines were a reaction product of the quartz grains inherent in the ash and the normal coal ash, with possible some contribution from acceptor fines.

Formation of the intermediate fines appears to be inevitable. Experience gained in pilot plant operations with seven different lignites and subbituminous coals showed that the as-built plant was operable without the need for auxiliary air to the gasifier, as long as the total SiO_2 content of the ash was less than 3 pounds per 100 pounds of moisture and ash-free coal.

In a commercial-sized system the intermediate fines problem will not exist, because these fines will be purged efficiently from the system. The regenerator will have a much lower bed height/bed diameter ratio than does the pilot plant regenerator and will be designed to have freeboard above the bed. This will allow the intermediate fines to be entrained overhead, along with the coal ash.

5.7.2.4   Deposits   (See Subsection 5.3.5)

Throughout the history of the pilot plant operation, deposits were observed to form in various plant vessels. Any time that it was believed that a deposit was the result of a process-related problem (as opposed to an occurrence related to a transient upset condition) an in-depth laboratory examination of the deposit was performed.

Generally the deposits associated with the plant can be divided into two types: The first type, agglomerates, were normally observed in the gasifier or boot where conditions were conducive to carbonation. Scanning electron microscopy, coupled with x-ray microanalysis studies of these agglomerates indicated that they formed via a mechanism involving the growth of calcium carbonate ($CaCO_3$) "necks" (Figure 5-34) between the discrete particles. Such growth can only occur in a static system; hence, under normal CO_2 acceptor plant operating conditions deposits of this type should not be able to form and thus should not be a problem.

The second general type of deposit observed during plant operation had the appearance of having been liquid at some time during formation. These deposits normally were associated with the regenerator and probably were a result of the formation of transient liquids.[3] Since deposit formation could always be linked to upset conditions, it should not be a problem in a smoothly operating plant.
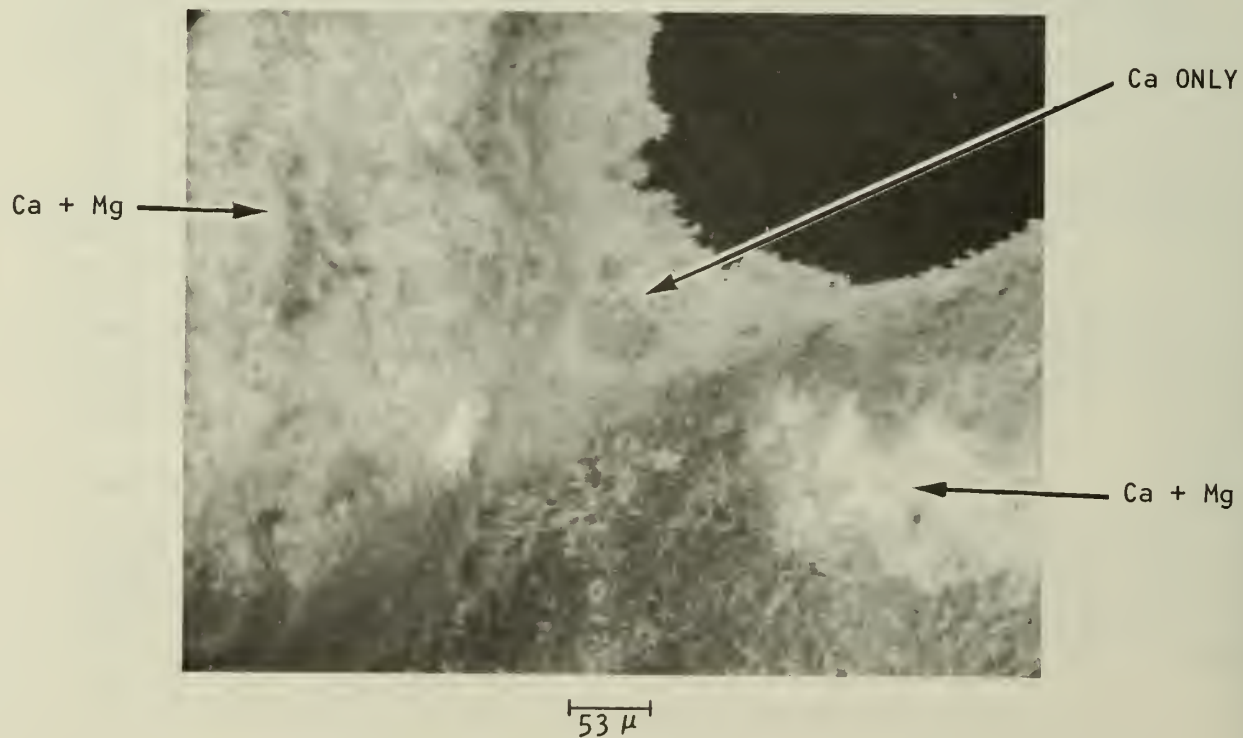
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(3)   Interim Rpt. No. 3, Book 3, Phase II, "Bench-Scale Research on CGS Process - Operation of the Bench-Scale Continuous Gasification Unit," January, 1970. Research and Development Report No. 16, National Technical Information Service PB-184720/AS.

Ca + Mg

Ca ONLY

Ca + Mg

$\overline{100\,\mu}$
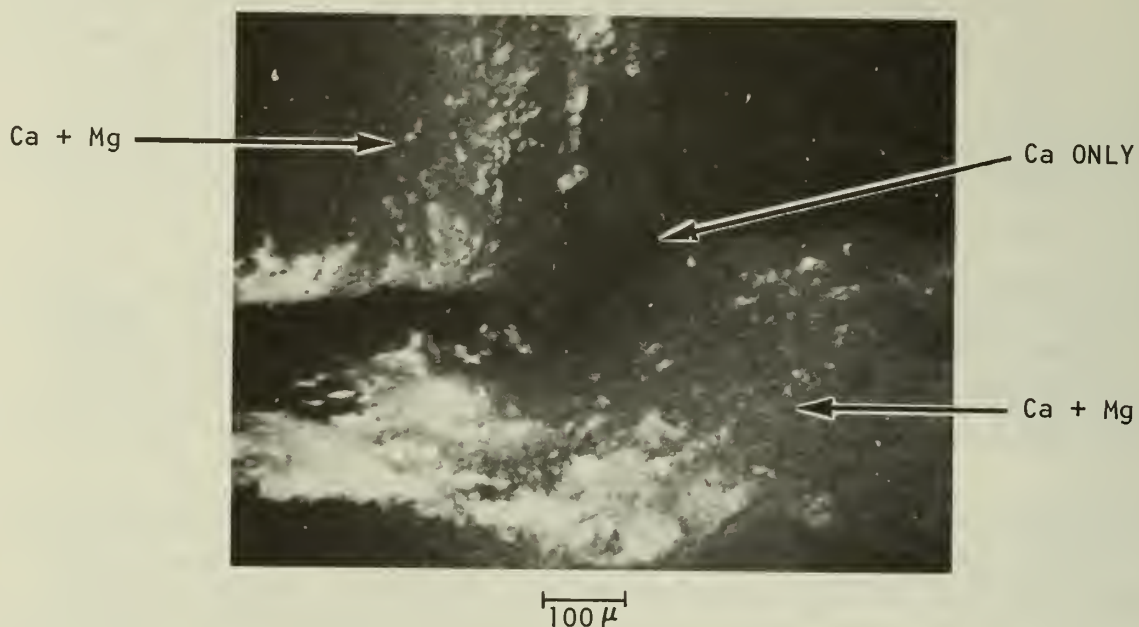
AGGLOMERATED ACCEPTOR PARTICLES - 100X

Ca ONLY

Ca + Mg

Ca + Mg

$\overline{53\,\mu}$

AGGLOMERATED DEAD BURNED DOLOMITE - 190X

Figure 5-34.   JOINTS BETWEEN AGGLOMERATED PARTICLES

One other type of deposit occasionally presented problems during plant operation. This consisted of deposits which formed on the walls of the calcined acceptor return leg from the regenerator and sometimes prevented acceptor circulation from being maintained. Laboratory work suggested that these deposits were the result of the recarbonation of acceptor fines in the standleg. This was possible since the temperature on the walls of the leg was low enough to permit calcium carbonate ($CaCO_3$) formation by the reaction of the calcined acceptor fines and CO_2 which was trapped between acceptor particles upon their exit from the regenerator. This problem was solved in the pilot plant by adding additional nitrogen gas purges to the return line.

5.7.3 OTHER SUPPORT WORK

A great deal of support work for the CO_2 acceptor process was carried out in order to find an acceptor which would have an economic advantage over natural stone acceptors. This effort can generally be divided into three separate studies: (1) synthetic acceptors, (2) reactivated acceptors, and (3) reconstituted acceptors.

5.7.3.1 Synthetic Acceptors

Early operations of the pilot plant revealed that the activity of the natural dolomite and limestone acceptors was considerably lower than had been anticipated from the earlier results of the bench-scale work. It would thus be desirable to find or produce an alternative acceptor which would maintain a higher level of activity for a much longer period of operation than the natural stones. An acceptor was envisioned which would have a calcium content such that its gravimetric factor, F_2, would be about 30% that of dolomite. If such a material were found, it may be possible to operate the gasifier under $CaCO_3$-$Ca(OH)_2$-CaO melt-forming conditions which would induce the complete recarbonation of the acceptor on each cycle, hence creating an acceptor of almost indefinite life.

Initial work was directed at attempting to impregnate CaO or $CaCO_3$ into the pores created by sintering MgO discs. This proved to be quite a difficult procedure and was soon abandoned.

Next, an attempt was made to create an in-situ matrix around the active calcium. This was accomplished by mixing finely divided silica (SiO_2) with a 30% excess of the calcium carbonate ($CaCO_3$) required for the formation of spurrite ($Ca_5(SiO_4)_2CO_3$). The powdered mixture was then pelletized and heated at 1600°F (871°C) in 1 atm of CO_2 gas. Under these conditions, all the silica reacts with calcium carbonate to form calcium monosilicate ($CaSiO_3$) which increases the strength of the pellets. The pellets were then ground, sized, and subjected to 18 atm of steam and 2 atm CO_2 gas at 1500°F (816°C), at which time the calcium silicate reacted with the calcium carbonate to form the spurrite matrix.

These calcium silicate-calcium carbonate synthetic acceptors were subjected to a series of tests in the automatic cycle test unit described

earlier, and it was found that cycling under $CaCO_2$-$Ca(OH)_2$-CaO melt-forming conditions does not lead to loss of particle identity and indeed does lead to virtually no loss of activity--even when cycled over 100 times, at which point natural limestone has essentially no activity. This type of synthetic acceptor could be of significant economic benefit in a commercial CO_2 acceptor process plant if reaction with coal ash can be avoided.

5.7.3.2   Reactivation of Spent Acceptor

Considerable time was spent on studies related to the reactivation of spent natural stone acceptors. Early work showed that while increased steam partial pressures led to slightly higher acceptor activities, this method would not lead to the significant increases in activity which were desired.

Other work on bed residence times indicated that no significant increases in acceptor activity could be gained by changing the acceptor residence times (within the range of times possible for plant operation) in either the gasifier or regenerator.

A method of reactivation was found that can lead to significant increases in activity; however, this method is quite sensitive to time and condition. The acceptor reactivation is the result of partial internal melting of individual particles by exposure to $CaCO_3$-$Ca(OH)_2$-CaO melt-forming conditions for very short time. If the time is short enough and the built-up shells thick enough, then it is possible to attain significant increases in acceptor activity by this method. It is unlikely, however, that this method would be of commercial value, due to the consequences of poor control of the time and pressures. Over-exposure of the acceptor to these melt-forming conditions leads to complete loss of particle identity and the formation of a pool of liquid.

5.7.3.3   Reconstituted Acceptors (See Section 6)

Various tests of reconstituted acceptor made from frozen melts in the $CaCO_3$-$Ca(OH)_2$ system were performed. The general conclusion from the studies of this material carried out in the automatic cycle tester is that such melts would be as suitable for use in the CO_2 acceptor process as fresh natural stone. The key to their use would hinge upon the economics of the production of this type of material versus the delivered costs of fresh stone.